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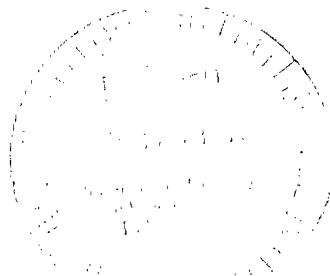
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COREST: A FORTRAN COMPUTER PROGRAM
TO ANALYZE PARALINEAR OXIDATION BEHAVIOR
AND ITS APPLICATION TO CHROMIC
OXIDE FORMING ALLOYS

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16. Abstract <p>A FORTRAN computer program (COREST) was developed to analyze the high-temperature par-linear oxidation behavior of metals. It is based on a mass-balance approach and uses typical gravimetric input data. COREST was applied to predominantly Cr_2O_3-forming alloys tested isothermally for long times. These alloys behaved paralinearly above 1100°C as a result of simultaneous scale formation and scale vaporization. Output includes the pertinent formation and vaporization constants and kinetic values of interest. COREST also estimates specific sample weight and specific scale weight as a function of time. Most importantly, from a corro-sion standpoint, it estimates specific metal loss.</p>				13. Type of Report and Period Covered Technical Note	
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COREST: A FORTRAN COMPUTER PROGRAM TO ANALYZE
PARALINEAR OXIDATION BEHAVIOR AND ITS APPLICATION
TO CHROMIC OXIDE FORMING ALLOYS

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SUMMARY

A FORTRAN program termed "COREST" has been developed for analyzing paralinear oxidation. It is based on the mass-balance expression ΔW (net sample weight change) = $W_r - W_m$. The W_r (specific weight of the retained oxide) and W_m (specific weight of the metal consumed) values can be generated independently as a function of time from a minimal amount of input weight change data, assuming that the type of oxide which forms is known. The W_m value is critical in corrosion. It is always increasingly greater with time in paralinear oxidation than in parabolic oxidation with the same parabolic scaling constant.

This technique of paralinear analysis was evaluated and demonstrated for predominantly Cr_2O_3 -forming alloys tested for long times above 1100°C . In general, experimental ΔW -against-time data agree quite closely with values estimated by the COREST paralinear program, usually within $\pm 0.5\text{ mg/cm}^2$. The derived paralinear scaling and vaporization rate constants k_p and k_v values were then used to predict long-time metal consumption for Cr_2O_3 /chromite-forming alloys in the 1000° to 1200°C range. Comparisons with parabolic oxidation data analysis show that the assumption of paralinear kinetics is more realistic for the alloys examined, particularly for long-time predictions. The paralinear model includes the parabolic, where the vaporization constant k_v approaches zero, as the limiting case. It is suggested that paralinear analysis be performed first on shorter time data to indicate how long a test should be run to meaningfully describe the oxidation behavior.

INTRODUCTION

The high-temperature, isothermal oxidation of metals and alloys is generally ana-

lyzed on the basis of oxygen weight gain as a function of time. This process follows parabolic kinetics if the oxide scale grows under conditions which are controlled by bulk diffusion. In this case, metal consumption with time can be calculated directly. In many cases, however, parabolic kinetics are not followed. For many high-chromium (Cr)-content, heat-resistant iron (Fe), nickel (Ni), or cobalt (Co) alloys, the scale formed is predominantly Cr_2O_3 . This oxide can further react with oxygen and volatilize according to the reaction $\text{Cr}_2\text{O}_3(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow 2\text{CrO}_3(\text{g})$ (ref. 1). This volatilization process is of special concern in the high-velocity environments that are encountered by orbital reentry vehicles and gas turbine engines. Thus, weight gains due to oxygen pickup and weight losses due to CrO_3 volatilization occur simultaneously. In this situation, the sum of the weight gain and weight loss processes does not produce a weight change curve that is parabolic with time. Therefore, metal loss (i.e., corrosion) cannot be directly estimated. Here, typical weight-change-against-time curves first increase to a maximum, then show a gradual weight loss, and finally exhibit an almost linear weight loss. Such behavior belongs to a general class of reactions that are termed "paralinear."

The paralinear reaction was defined by Haycock (ref. 2) for a barrier scale layer being formed by diffusion and simultaneously being depleted at a constant rate by a secondary process. Haycock derived a general solution for the rate equation, and Wajszel (ref. 3) solved it specifically for a diffusion-controlled, volatile-scale-formation case. More recently, beginning with Tedmon (ref. 4), Giggins and Pettit (ref. 5), Lewis (ref. 6), Stringer (ref. 7), and Ecer and Meiser (ref. 8), the problem of analyzing paralinear data and deriving the proper constants has been investigated. Because of the nature of the equations, the experimental data are difficult to interpret and analyze unless a convenient computer program is available.

This report presents a computer program that can be used to analyze and extrapolate paralinear oxidation data in a convenient, readily usable form. This program, called COREST, is flexible enough so that it can be used under various conditions of oxidation testing and analysis and still estimate corrosion attack. In this report, paralinear oxidation analysis and the COREST computer program are described in detail. The COREST program is then applied to the analysis of the long-time oxidation test results for various Cr_2O_3 /chromite-forming alloys that were available in the literature or that were obtained at this laboratory.

Included is a comparison of how well the calculated specific weight change values match the experimental data points depending on whether short-, middle-, or long-time input data are used. The comparison is intended to answer the critical questions - how long should an oxidation test be run to properly interpret oxidation behavior and how can one make the distinction between parabolic and paralinear kinetics?

Finally, the derived rate constants are used in the COREST program to estimate the long-time (100 000 hr) oxidation behavior of Cr_2O_3 /chromite-forming alloys in the 1000°

to 1200° C range, with emphasis on metal consumption. These estimates assume that parabolic kinetics still control oxidation at times beyond 10 000 hours. These estimates were made for the most and the least oxidation resistant of the predominantly Cr₂O₃-forming alloys considered for several airflow (i.e., vaporization) conditions. Long-time oxidation behavior estimates were also made by assuming parabolic kinetics, and the results were compared with those obtained from the COREST program.

SYMBOLS

A	parabolic scaling constant for oxidation in terms of weight of metal consumed (not the usual weight of oxygen picked up), (mg/cm ²) ² /hr (So in terms of the rate constant k_p in the oxidation literature, $A = a^2 k_p / 2$.)
a	stoichiometric constant; ratio of atomic weights of metal to oxygen in the oxide (For Cr ₂ O ₃ , $a = (52.00 \times 2) / (16.0 \times 3) = 2.1667$.)
B	specific linear weight loss rate for the metal in the volatile oxide on the sample per unit of time, mg/cm ² /hr
b	stoichiometric constant; ratio of molecular weight of oxide to oxygen in the oxide (For Cr ₂ O ₃ , $b = (52.00 \times 2 + 16.0 \times 3) / (16 \times 3) = 3.1667$. It can be shown $b = a + 1$.)
k_p	conventional parabolic scaling constant in terms of weight of oxygen picked up, $k_p = \frac{2A}{a^2}$, (mg/cm ²) ² /hr
k_v	linear weight loss rate due to vaporization of the oxide formed on the sample, $k_v = \frac{b}{a} \times B$, mg/cm ² /hr
t	time, hr
\bar{t}	time to reach $\bar{\Delta W}$ in parabolic oxidation, hr
t_0	time for ΔW to return to zero in parabolic oxidation (i.e., the zero cross-over time)
W_m	specific weight of metal consumed per unit area due to oxide buildup <u>and</u> scale vaporization at any time t, mg/cm ²
W_r	specific weight of metal oxide formed and retained on the metal sample to any time t (termed W_p in ref. 3), mg/cm ²
$W_{r, \text{lim}}$	limiting (maximum) value of W_r in parabolic oxidation, mg/cm ²

ΔW	specific sample weight change at any time t , mg/cm^2
$\Delta \bar{W}$	maximum ΔW reached in parilinear oxidation (termed \bar{W} in ref. 3)
$\left. \begin{array}{l} \Delta W_1, t_1 \\ \Delta W_2, t_2 \end{array} \right\}$	data sets of observed ΔW 's and their corresponding times
ρ_m	aggregate average density of the metal(s) consumed in the total oxidation process, g/cm^3
ρ_r	density of the oxide formed and retained in oxidation, g/cm^3

PARILINEAR ANALYSIS

For conventional diffusion-controlled parabolic oxidation, the basic equations are

$$\Delta W = k_p^{1/2} t^{1/2} \quad (1)$$

$$W_m = a k_p^{1/2} t^{1/2} \quad (2)$$

and

$$W_r = b k_p^{1/2} t^{1/2} \quad (3)$$

Thus W_m , the critical attack parameter in oxidation corrosion, is implicit in equation (1) assuming, as is almost always the case, that the type of alloy and the composition of its scale are known. All pertinent corrosion estimates can therefore be derived by simple weight change measurements.

In parilinear oxidation, two simultaneous processes are occurring: diffusion-controlled oxide buildup and loss by such linear processes as scale vaporization and/or isothermal scale spalling. An equation analogous to equation (1) can be written for specific sample weight change in the approximate form based on the two simultaneous processes,

$$\Delta W = k_p^{1/2} t^{1/2} - k_1 t \quad (4)$$

(where k_1 is a general linear constant), but no analogous expressions can be written

directly for W_m or W_r for this parilinear model.

Wajszel, however, in a little noted paper (ref. 3) has started from the basic mass-balance equation for any oxidation process,

$$\Delta W = W_r - W_m \quad (5)$$

and solved the basic differential equations for W_r and W_m separately. These two values can then be combined in equation (5) to give the ΔW for any set of paired solutions for W_r and W_m at any time. Therefore, for the basic parilinear model, this method gives the exact solution as a function of time for ΔW , W_m , and W_r .

The basic equations for W_m , W_r , and ΔW derived by Wajszel can be generalized by dimensional analyses (ref. 9), as described in appendix A. This approach makes computer analysis of the parilinear process reasonably straightforward.

The fundamental differences between the two basic oxidation reactions - parabolic and parilinear - are shown in figure 1 in terms of ΔW , W_m , and W_r for hypothetical alloys with identical k_p 's but with different k_v 's. For example, $a = 2.0$ and $k_p = 0.1 \text{ (mg/cm}^2\text{)}^2\text{/hr}$ for both; but in one case, $k_v = 0.05$, while in the other case, $k_v = 0.00001 \text{ mg/cm}^2\text{/hr}$. The latter k_v is approximately 0, or the parabolic case in the limit. The basic differences are shown on the plot. Not only are the curve shapes drastically different, but more importantly in terms of the specific weight of metal consumed W_m , in the parilinear case the value at 1000 hours is almost twice that of the parabolic case. This difference is even more extreme at longer times.

FOUR TYPES OF INPUT DATA FOR PARILINEAR OXIDATION SOLUTIONS

Based on the solution to the equations outlined in appendix A, four cases can be presented that cover the major types of analyses for parilinear oxidation data. It is assumed that the major type of oxide formed has been identified and that therefore the stoichiometric constants a and b are known. For the four types of input data described here, all parilinear constants of interest can be calculated - including k_p , k_v , and crossover times. Values for ΔW , W_m , and W_r can be computed for any desired time. The weight change values can be converted to estimated thickness changes when the densities of the metal and scale are known.

The four types of input data are

Type 1 - The input values are the maximum positive specific weight change $\Delta \bar{W}$ and the time to reach that value \bar{t} .

Type 2 - The input values are the parabolic scaling constant k_p and linear vaporization constant k_v .

- Type 3 - The input values are either k_p or k_v and any one set of weight change and time point (e.g., $\Delta W_1, t_1$).
- Type 4 - This is the most general case. Two sets of weight change and time points ($\Delta W_1, t_1$ and $\Delta W_2, t_2$) are the necessary input. This case is commonly used when a specific weight-change-against-time plot is available that extends well into the negative weight change region. Here the input can include the last data point along with an estimate of the exact time when the ΔW equaled zero (i.e., the zero crossover point).

FORTRAN PROGRAM (COREST)

The program, shown schematically in figure 2, consists of the following 14 sub-routines:

- (1) MAIN is the executive routine for processing multiple cases and has primary control of logical flow throughout the complete program.
 - (2) BLOCK DATA reads initial conditions, parameters, and other data required for internal use by the program (looping indices, etc.).
 - (3) BEGIN has charge of initial computations for use by the rest of the program, reads program descriptors from cards, and does initial printouts.
 - (4) STOICH calculates the α and β coefficients for the program.
 - (5) ZERO calculates the dimensionless crossover time and the time ratio value of the crossover point to the point of maximum net weight.
- The following four QUERY routines determine the numerical values of the parilinear parameters from among several possible types of input data:
- (6) QUERY1 - ITYPE = 1; input arguments, $\Delta \bar{W}$ and \bar{t}
 - (7) QUERY2 - ITYPE = 2; input arguments, k_p and k_v
 - (8) QUERY3 - ITYPE = 3; input arguments, k_p or k_v and any weight-change-against-time pair ($\Delta W_1, t_1$)
 - (9) QUERY4 - ITYPE = 4; input arguments, two weight-time pairs ($\Delta W_1, t_1$; $\Delta W_2, t_2$)
 - (10) OUTPUT calls subroutines for computing the net specific weight curve and controls printout of results.
 - (11) SPEVAL calculates certain weights at special times of interest: $\bar{W}_m, W_{m,0}, \bar{W}_r, W_r, \lim$
 - (12) PROVAL calculates the times at which the sample reaches required fractions of the limiting specific scale weight.
 - (13) CORODE calculates the times at which the sample suffers certain levels of metal loss by corrosion.

(14) CURVE, a principal subprogram, computes the corrosion history of the sample.

The FORTRAN program is listed in appendix B, FORTRAN symbols are defined in appendix C, and an example for an experimental case based on type 4 input is presented in appendix D. For this example, the total computer time was 23.6 seconds on a UNIVAC 1110.

USING THE PROGRAM

Data input to the program is primarily through the BLOCK DATA subprogram (fig. 3). After the card "Input follows," come the actual block data input cards for a given series of runs. The contents of each of these cards are as follows:

Card 1 - DATA ASMALL,BSMALL: The stoichiometric constants a and b for a given oxide are listed here. The a value is available in table I for most oxides of interest; $b = a + 1$.

Card 2 - DATA ITYPE,LL,LLX: The ITYPE values of 1, 2, 3, or 4 specify one of the four types of parilinear solutions desired. LL denotes the number of time values (up to 100) for which W_m , ΔW , W_r , etc., are to be calculated. LLX specifies the number of time values (to 10) to be calculated to reach certain preselected values of W_m .

Card 3 - DATA NUMSET: The number of runs to be computed (to 100) is designated.

Card 4 - DATA QP: A series (to 10) of decimal fractions of $W_{r,lim}$ are given for which the corresponding times are to be computed.

Card 5 - DATA XXX: A series of values in mg/cm^2 are given for which the corresponding times in hours to reach these values are to be computed. The number of these values listed is equal to the LLX value on card 2.

Card 6 - DATA HOURS: The individual time values in hours are listed for which the corresponding ΔW , W_m , W_r , and thickness changes are to be calculated. The number of values listed is equal to the LL value on card 2.

Cards 7 and 8 will depend on the DATA ITYPE of card 1.

Card 7 (type 1) - DATA WBAR: A sequential series of $\Delta \bar{W}$ values in mg/cm^2 are given, with the number of values equal to the NUMSET value on card 3.

Card 8 (type 1) - DATA TBAR: A sequential series, to match card 7, of \bar{t} values in hours are given, with the number of values equal to the NUMSET value on card 3.

Card 7 (type 2) - DATA XKP: A sequential series of k_p values in $(\text{mg}/\text{cm}^2)^2/\text{hr}$ is given, with the number of values equal to the NUMSET value on card 3.

- Card 8 (type 2) - DATA XKV: A sequential series, to match card 7, of as many as 100 k_v values in $\text{mg}/\text{cm}^2/\text{hr}$ are given, with the number of values equal to the NUMSET value on card 3.
- Card 7 (type 3) - DATA NUMKP or DATA NUMKV: Contents are similar to those of card 7 (type 2) and card 8 (type 2).
- Card 8-1 (type 3) - DATA WW: A sequential series of single ΔW values in mg/cm^2 at any time are given, to be used with either k_p or k_v in the same sequence.
- Card 8-2 (type 3) - DATA TT: A sequential series of single-time values t in hours are given which match the corresponding ΔW values on card 8-1. These sets of $\Delta W, t$ values are used with the corresponding k_p or k_v . The number of corresponding data sets is equal to the NUMSET value on card 3 multiplied by the NUMKP or NUMKV value on card 7.
- Card 7 (type 4) - DATA WW: A series of paired ΔW values (as many as 100) in mg/cm^2 at any two times are given, with the number of paired values equal to the NUMSET value on card 3.
- Card 8 (type 4) - DATA TT: A series of paired time values t (as many as 100) in hours are given for the corresponding ΔW values on card 7. The number of paired values is equal to the NUMSET value on card 3. At program execution, five additional input cards are read.
- Card 1A - TRUE or FALSE is punched starting in column 1. FALSE means that the term "vaporization" will be used in the headings. TRUE means that the term "spalling" will be used in the headings.
- Card 2A - (Format 6A6, F6. 3): A description of the alloy type(s) for the series of run(s) printed at the heading of each run is followed by the aggregated average density of the alloy being consumed, in g/cm^3 . This density is used to calculate the effective thickness change of the alloy based on attack from one side.
- Card 3A - (Format 6A6, F6. 3): A description of the scale type(s) for the series of run(s) printed at the heading of each run is followed by the estimated density of the oxide remaining on the alloy, in g/cm^3 . This density is used to calculate the scale thickness of the oxide.
- Card 4A - (Format 8A6, 2A6): A description of the data source(s) and the series of runs is printed at the heading of each run.
- Card 5A¹ - (Format 2A6, 2A6): A description of the test temperature(s) and test pressure(s) is printed at the heading of each run.

¹Card 6A - Plotting routine called (T) or not called (F) with subroutine supplied by user at particular installation.

An example of this input is shown in figure 3 for a type 4 input of two runs. This means there are two sets of paired $\Delta W_1, t_1$ and $\Delta W_2, t_2$ input values. There are 17 time values ranging from 0.31 to 236.11 hours for which the ΔW , W_m , W_r , and thickness change calculations are to be made. The times to reach three different fractional specific weights (0.5, 0.90, and 0.95) of the limiting-scale specific weight are requested, as well as the times to reach three values of W_m . The output listing is presented in appendix D.

APPLICATION OF COREST TO THE OXIDATION BEHAVIOR OF

Cr_2O_3 /CHROMITE-FORMING ALLOYS

The basic COREST program has been used previously by NASA authors with type 3 input (with a set of $\Delta W_1, t_1$ values and an estimated k_v) to analyze Cr_2O_3 /chromite-forming alloys tested isothermally at 1150° C for 100 hours (ref. 10). It is inferred in this reference that under these test conditions the alloys were oxidizing according to the parilinear model but that $\Delta \bar{W}$ occurred well beyond the 100-hour limit of the tests conducted. Even though the degree of fit appeared excellent, it was desired to examine test data where $\Delta \bar{W}$ had actually been reached and preferably where t_0 , the zero crossover point, had actually been observed. The literature for classic Cr_2O_3 /chromite-forming alloys (i.e., class II formers in ref. 10) showed two such examples (refs. 4 and 6).

For this reason, four supplemental tests were performed on two additional alloys at this laboratory for times long enough so that at least the zero crossover point was approached. This testing was conducted basically to determine how well the early ($<\bar{t}$), middle ($\sim\bar{t}$), and later ($>\bar{t}$) time parts of the curve establish the rest of the ΔW -against-time plot and how their use changes the long-time predictions ($>10\,000$ hr). The parilinear model, assuming it still holds, is thought to be more realistic than the parabolic model.

The data from the two literature and four NASA Lewis runs used for input into COREST are shown in table II. Data on Cr-0.2Y were taken from reference 4, and data on Ni-20Cr-3Fe-0.4Si (termed "Alloy A") were taken from reference 6. Both alloys were tested in static air at 1200° C. The tests performed at this laboratory were on Ni-40Cr and Tophet 30 (Ni-29.6Cr-1.4Si) at 1200° C in static air. In addition, duplicate tests were run on Tophet 30 at 1150° C in static air.

The six experimental ΔW -against-time plots are shown in figures 4 to 9 with the observed data points plotted as circular symbols. Also shown on each plot (square symbols) are the COREST-generated ΔW -against-time plots derived from the type of input

data that gives the lowest error of estimate.²

Table III shows the degree of fit based on the minimum error of estimate calculated between the observed values and each comparable COREST-calculated data point. Also listed are the various parilinear parameters of interest: k_p , k_v , $\Delta\bar{W}$, and t_0 and the predicted t for W_m to reach 71.9 mg/cm² (i.e., 100 μ m of metal consumption). Finally, the critical W_m values are plotted in figure 10 for times longer than 1000 hours for each of the six alloys. The W_m values plotted for each alloy are those representing the best degree of fit.

RESULTS AND DISCUSSION

The specific weight change curves for the six experimental runs are plotted in figures 4 to 9 as a function of time, along with the COREST-calculated ΔW values. These runs are summarized in table III, which lists the three time stages of input data from table II, as well as the various derived parilinear constants and other values of interest such as selected estimates of certain t and W_r values. The degree of fit between the derived and actual curves is given as an average error of estimate in mg/cm². These cases were derived either from a type 1 calculation, where the curve maximum was estimated, or from the more general type 4 calculation used both for the pre- and post- $\Delta\bar{W}$ cases. The degree of fit is good - usually less than ± 0.5 mg/cm² even for the longer runs.

The degree-of-fit criterion is given in terms of an average error of estimate of the calculated ΔW curve compared with the experimental ΔW curve. It was used to determine how long, in general, a parilinear test must be run to give meaningful long-time estimates of W_m . Obviously, from a practical point of view, a shorter (before $\Delta\bar{W}$) 100- to 200-hour test is to be preferred. However, as the degree-of-fit criterion indicates, the tests should at least be run to $\Delta\bar{W}$ - and preferably into the negative slope region. Using input values before $\Delta\bar{W}$ does, however, at least result in more pessimistic long-time W_m estimates than the $\Delta\bar{W}$ or post- $\Delta\bar{W}$ cases. On the other hand, if parabolic oxidation is assumed, which has usually been the case, the long-time W_m values are drastically underestimated, as shown in figure 10.

An example of how the assumption of parabolic kinetics can influence the interpretation of parilinear oxidation data is shown in figure 11. If the Alloy A oxidation test dis-

$$\left[\frac{\sum (\Delta W_{i, \text{exp}} - \Delta W_{i, \text{calc}})^2}{\text{Number of } \Delta W \text{ values}} \right]^{1/2} = \text{Average error of estimate}$$

cussed previously had been only 300 hours long rather than the actual 1000 hours, the resulting data plotted on a $(\Delta W)^2$ -against-time plot³ would appear to represent two-stage parabolic oxidation. The derived parabolic constants, if then used to estimate metal loss, would give a W_m at 1000 hours of about 16.5 mg/cm². If only the higher first-stage constant were used, metal loss would be about 20.7 mg/cm². However, based on the full 1000-hour curve with the vaporization of Cr₂O₃ leading to paralinear behavior, the W_m estimate is 32.61 mg/cm², almost twice the original estimate. Extrapolated to 10 000 hours, this ratio of underestimated loss would be almost 5:1. On the other hand, if short-time data were used in a type 4 paralinear analysis, a greater W_m value would actually be estimated at 1000 hours than when the negative slope values were used. This is the most conservative estimate and probably the safest from a design standpoint if the W_m values are converted to an effective thickness change. It has the obvious advantage that a test would not have to be run out to a weight loss situation.

The long-time comparisons for Alloy A using all three of the basic attack variables - ΔW , W_r , and W_m - are shown in figure 12 for both the parabolic and paralinear (calculated) cases, assuming the same k_p . This log-log plot graphically shows that as the scale specific weight approaches about 90 percent of its limiting scale specific weight of 64.5 mg/cm², the W_m value rises sharply and the ΔW drops sharply (toward negative values).

The calculated k_p values (based on input values with the best fit) are replotted as a function of the reciprocal of the absolute temperature in figure 13. The k_p values fall in the range for conventional Cr₂O₃-forming alloys, which is discussed in reference 10. These were also calculated by COREST but based mostly on shorter time (100 hr) exposure data. The k_p results for Tophet 30 fall slightly below the lower limit for the Cr₂O₃/chromite range. It is believed that the relatively high Si content in Tophet 30 causes the erratic early paralinear oxidation behavior as well as the lower consumption rate after $\Delta \bar{W}$. Silicon dioxide (SiO₂) in the scale apparently behaves like thorium dioxide (ThO₂) blockage in TD-NiCr alloys, lowering the effective k_p (ref. 10).

The derived paralinear k_v values (again based on input values with the best fit) are plotted in figure 14 against $1/T_K$, along with other pertinent k_v values derived for the vaporization of bulk Cr₂O₃. This figure shows k_v values derived gravimetrically by Hagel (ref. 11) for sintered Cr₂O₃ tested in still air, along with the limits for 1 standard deviation. The k_v value of a sintered Cr₂O₃ sample run at this laboratory as a check falls almost exactly on Hagel's value. This implies that test conditions were comparable and that condensation of Cr₂O₃ on the balance hanger wire did not significantly bias the derived results. Also plotted in figure 14 are literature values for vaporization of Cr₂O₃ prepared by sintering or hot pressing both in static and moving air (ref. 12)

³The slope of the $(\Delta W)^2$ -against-time plot is the usual graphical method used to derive parabolic scaling constants.

and for vaporization of stripped Cr_2O_3 scales from an oxidized Ni-50Cr alloy (ref. 8). Ecer and Meiser (ref. 8) also calculated a minimum vaporization rate in static oxygen at 1 atmosphere based on gaseous diffusivity. Of interest from a practical point of view is the maximum possible loss rate of Cr_2O_3 . Such loss can be determined from the vapor pressure of CrO_3 at the partial pressure of oxygen in 1-atmosphere air by using the Langmuir equation and vapor pressure data for CrO_3 cited by Kohl and Stearns (ref. 13). Obviously, this is a limiting case with a Cr loss rate some 4 orders of magnitude higher than that observed in static air. The k_v loss rate in a high-velocity burner rig test on a Cr_2O_3 -forming alloy should be intermediate between these limiting values but as yet is undetermined. As the upper limit is approached, the Cr consumption rates would be so high, particularly in the higher temperature regions, that the Cr would probably be depleted, which would favor NiO and increased chromite spinel formation. In cyclic oxidation these scales would spall catastrophically (ref. 14), which would result in accelerated attack.

It can be seen that these calculated k_v values can vary widely at a given temperature between the upper and lower estimated limits - over 5 orders of magnitude. Most laboratory tests, whether in still or moving air, appear to be within a factor of 10 in the lower third of the range. It was thought that, in the static-air tests, the parabolic k_v values were lower than Hagel's bulk values because NiO and/or spinel overlay the Cr_2O_3 (ref. 10). However, the scatter may be due to experimental variation. It does appear that the derived k_v values for the three Tophet 30 runs are somewhat lower than those for the other alloys cited. If these are real differences, the implication in terms of overall attack (i.e., W_m) is that Tophet 30 is even more oxidation resistant in static air than the general class of Cr_2O_3 /chromite-forming alloys.

It is critical, particularly for a practical test situation, to determine how long a test exposure should be run before deciding that the oxidation behavior is parabolic rather than parabolic. For Cr_2O_3 /chromite-forming alloys, figure 13 shows that k_p values can range from just over 10^{-3} to just over 10^0 $(\text{mg}/\text{cm}^2)^2/\text{hr}$, in the temperature range 1000° to 1200° C. From figure 14 the lower range of k_v values in static air is from about 10^{-3} $\text{mg}/\text{cm}^2/\text{hr}$ at 1000° C to as high as 1.0 $\text{mg}/\text{cm}^2/\text{hr}$ at 1200° C. These ranges of k_p and k_v values were combined in a series of COREST calculations to predict \bar{t} , the time to reach $\Delta\bar{W}$. This is the minimum test time to determine parabolic behavior. Because the inflection tends to be gradual and ΔW returns to the origin (0.0 mg/cm^2) at just over four times the predicted \bar{t} , running the test to twice the predicted \bar{t} seems reasonable to accurately determine the behavior.

This approach is summarized in figure 15, which shows the critical nature of k_v values between 10^{-3} and 10^{-2} $\text{mg}/\text{cm}^2/\text{hr}$. The series of curves imply that for virtually all k_v values of 10^{-3} or less the behavior is effectively parabolic for most practical exposure situations. Above k_v values of about 5×10^{-2} mg/cm^2 the kinetics are

obviously parilinear for test times of just a few hundred hours. For k_v values between 10^{-3} and 5×10^{-2} mg/cm²/hr, figure 15 can be used in conjunction with the end application to determine a meaningful test time. Obviously, for tests in a moving-air environment the k_v values shift to the higher values in figure 14, where parilinear behavior is apparent at much shorter test times.

Figure 16 shows how this parilinear approach might be used to estimate long-time oxidation damage over a wide range of temperatures. From figure 13, upper and lower limit values of k_p for predominantly Cr₂O₃-forming alloys were estimated at 50-degree intervals from 1000° to 1200° C. From figure 14, for each of these temperatures three values of k_v were estimated, representing the likeliest static-air value, 10 times this value (representing moving air), and the maximum possible k_v derived from the Langmuir equation for free vaporization (ref. 13). These values of k_p and k_v were combined in the six possible combinations as the input values in the COREST program to generate ΔW , W_m , and W_r as a function of time. A plotting subroutine was then used to plot W_m as a function of time on a log-log plot at times longer than 10 000 hours. The pertinent data (except for the free-vaporization case) are summarized in table IV. These curves are based on the assumption that parilinear behavior continues beyond 10 000 hours, which implies continued Cr₂O₃/chromite control. However, if the base metal oxide becomes rate controlling because of previous Cr depletion, earlier catastrophic failure is apt to occur from spalling - particularly if thermal cycling is involved. The parilinear estimate is still more realistic than that derived from the parabolic model. However, comparable parabolic plots on a log-log scale would be straight lines with a slope of 0.5.

At all temperatures, when the Langmuir vaporization rate is the controlling factor, the overall loss rate is effectively a linear process. In this case the ratio of k_v to k_p is so great that the scale has a limiting thickness of well under a micrometer. This ratio is close to 0.01 with the low-range k_p 's and equal to 0.25 with the high-range k_p 's. When the k_v value is increased by a factor of 10, the limiting scale thickness drops by a factor of 10, and the time to consume a given amount of Cr decreases by a factor of 100. Thus, the metal consumption rate seems to increase with the square of the ratio of the vaporization rates. Parabolic scaling constant ratios, on the other hand, affect metal consumption rates in strictly a linear manner. The times to reach a given W_m show the striking differences at all temperatures between the parilinear and parabolic cases. Ratios are as high as 39:1 for $W_m = 719$ mg/cm² (~ 1000 μ m) for even the static-air case.

CONCLUDING REMARKS

The oxidation behavior of four predominantly Cr₂O₃-forming alloys oxidized for

long times above 1100° C was analyzed by comparing the observed net-weight-change-against-time values with their corresponding calculated values, assuming parilinear behavior. The calculated values were generated by the COREST computer program based on short-time input before the obvious $\Delta\bar{W}$, at the estimated $\Delta\bar{W}$, and after the $\Delta\bar{W}$ on the downslope of the curve, where parilinear behavior is clearly established. The agreement between the calculated and observed ΔW values on the average was $\pm 0.5 \text{ mg/cm}^2$. Based on the degree of fit as might be expected, long-time input data are preferable. However, even the use of short-time input data, assuming parilinear behavior, is more meaningful than assuming parabolic scaling kinetics. The latter method greatly underestimates the critical W_m values particularly at longer times. Based on these results, it is suggested that the parilinear assumption be used to analyze any short-time data since it includes the parabolic case as a limit with $k_v \rightarrow 0$. The k_v is effectively zero if it is $< 0.001 \text{ mg/cm}^2/\text{hr}$, provided k_p is greater than about $0.01 (\text{mg/cm}^2)^2/\text{hr}$. In this case the behavior is essentially parabolic and the test can be terminated.

Based on the range of derived k_p and k_v values for Cr_2O_3 /chromite-forming alloys, a series of curves have been derived for the critical corrosion parameter W_m at 1000°, 1050°, 1100°, 1150°, and 1200° C for times to 10 000 hours and beyond. The six curves generated at each temperature represent the highest and lowest k_p values, along with three k_v values - the likeliest static-air value, 10 times this value (which represents moving air), and a maximum k_v derived from the Langmuir equation for free vaporization. The curves reflect the strong effect of vaporization, particularly in moving air.

The COREST parilinear mass-balance approach is currently being used in analyzing cyclic oxidation where scale spalling, as well as oxide vaporization, can occur. The COREST approach appears quite promising for those alloys where the spalling rate appears fairly uniform over a number of test cycles.

SUMMARY OF RESULTS

A FORTRAN computer program termed COREST has been developed for analyzing parilinear oxidation based on the mass-balance expression ΔW (net sample weight change) = $W_r - W_m$. The W_r (specific weight of the retained oxide) and W_m (specific weight of the metal consumed) values can be generated independently as a function of time from a minimal amount of input data with a known scale. The W_m value is critical in corrosion, and the W_m values in parilinear oxidation are always increasingly greater with time than the corresponding values for parabolic oxidation. The COREST program also converts W_r and W_m to thickness values with suitable input of

oxide and metal density values. With a stoichiometric constant calculated from the composition of the oxide, the following four types of input data can be completely analyzed by COREST:

- (1) The maximum estimate value of ΔW and its corresponding time
- (2) Any paired values of the parabolic scaling constant k_p and linear vaporization rate constant k_v (where $k_v \neq 0$)
- (3) Any value of k_p or k_v , along with any one set of ΔW with its corresponding time
- (4) Any two sets of ΔW values with their corresponding times

From these four types of input the program calculates and lists

- (1) k_p and k_v
- (2) The maximum positive ΔW and its corresponding time and W_m and W_r
- (3) The time for ΔW to return to zero and its corresponding W_m and W_r
- (4) The limiting value of W_r and its corresponding thickness
- (5) The time(s) to reach any requested fraction(s) of the limiting value of W_r
- (6) The time(s) to reach any requested value(s) of W_m
- (7) The ΔW , W_m , W_r , effective metal thickness loss, and oxide thickness for any requested time(s)

The derived parilinear scaling constants for straightforward chromic oxide (Cr_2O_3)/chromite-forming alloys generally fall within the range of the previously published values of k_p . The derived k_v values increase as expected with increasing temperature but are less than the k_v values for bulk Cr_2O_3 in static air. This difference is greater in NiCr alloys than in pure Cr presumably because of a thin NiO and/or chromite spinel layer on the outer surface which probably spalls on cooling.

The presence of 1.5 percent silicon in Tophet 30 appears to lead to silicon dioxide blockage in the Cr_2O_3 scale. This apparent blockage causes the initial k_p to drop until the time to reach $\Delta \bar{W}$, the maximum ΔW reached in parilinear oxidation, is exceeded and thus leads to lower than expected metal consumption rates.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 30, 1975,
505-01.

APPENDIX A

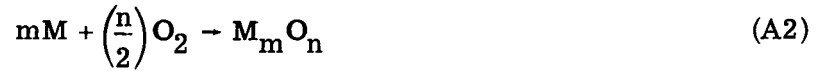
ANALYTICAL EQUATIONS AND COMPUTER PROGRAM

Derivation and Solution of the Paralinear Equations

The analysis anticipates a type of metal oxidation experiment from which the basic data consist of a history of sample weights taken at a progression of discrete times and a knowledge of the stoichiometric conversion factor from metal to oxide scale. For those systems that suffer scale loss by vaporization, the mass balance for the sample states that

$$\left[\begin{array}{c} \text{Total sample} \\ \text{weight change} \end{array} \right] = \left[\begin{array}{c} \text{Weight of} \\ \text{scale produced} \end{array} \right] - \left[\begin{array}{c} \text{Weight of} \\ \text{metal oxidized} \end{array} \right] - \left[\begin{array}{c} \text{Weight of} \\ \text{scale vaporized} \end{array} \right] \quad (\text{A1})$$

Now, for the metal-oxidation reaction,



the stoichiometric conversion factor a is defined as

$$a = \frac{m \left[\begin{array}{c} \text{Atomic weight of} \\ \text{metal, } M \end{array} \right]}{\left[\begin{array}{c} \text{Molecular weight of} \\ \text{scale, } M_m O_n \end{array} \right] - m \left[\begin{array}{c} \text{Atomic weight of} \\ \text{metal, } M \end{array} \right]} \quad (\text{A3})$$

As an example, $a = 2.1667$ for chromic oxide (Cr_2O_3). The ratio of the weight of scale formed to the weight of metal oxidized is

$$\frac{\left[\begin{array}{c} \text{Molecular weight of} \\ \text{scale, } M_m O_n \end{array} \right]}{m \left[\begin{array}{c} \text{Atomic weight of} \\ \text{metal, } M \end{array} \right]} \quad (\text{A4})$$

Replacing the scale weight term in the mass-balance equation (A1) by the oxidized metal weight times the ratio (A4) yields

$$\begin{aligned}
\left[\begin{array}{c} \text{Total sample} \\ \text{weight change} \end{array} \right] &= \left[\frac{M_m O_n}{mM} - 1 \right] \left[\begin{array}{c} \text{Weight of} \\ \text{metal oxidized} \end{array} \right] - \left[\begin{array}{c} \text{Weight of} \\ \text{scale vaporized} \end{array} \right] \\
&= \frac{1}{a} \left[\begin{array}{c} \text{Weight of} \\ \text{metal oxidized} \end{array} \right] - \left[\begin{array}{c} \text{Weight of} \\ \text{scale vaporized} \end{array} \right]
\end{aligned} \tag{A5}$$

The time derivative of equation (A5)

$$\frac{dW}{dt} = \frac{1}{a} \frac{dW_m}{dt} - \frac{dW_s}{dt} \tag{A6}$$

is the mass-balance rate equation that is the starting point for subsequent analyses of the metal oxidation history.

By using the parabolic rate term of Haycock (ref. 4) for dW_m/dt and a linear vaporization rate for dW_s/dt , Wajszel (ref. 3) was able to integrate equation (A6). This solution for sample weight as a function of time was termed paralinear by Wajszel because of its dependency on the parabolic oxidation model and the linear scale vaporization model.

Paralinear oxidation model. - This is an Ohm's law analogy. The flux of oxygen ions through a unit cross-sectional area to the scale-metal interface is inversely proportional to the length of the flux path (i.e., scale thickness). The proportionality constant is the paralinear conductance of Haycock.

Since the rate of metal oxidation equals the flux of oxygen ions, Wajszel expresses this fact within the Ohm's law model as

$$\frac{dW_m}{dt} = \left(\frac{b}{a} \right) \frac{A}{W_r} \tag{A7}$$

where the weight of scale⁴ per unit area W_r is equivalent to the scale thickness, the proportionality constant A contains the paralinear conductance, and the factor b/a is the molecular weight ratio of scale weight to metal weight.

Linear scale vaporization model. - The simplest model one can devise for loss of scale by vaporization postulates a rate that is independent of time for a given set of experimental conditions. In other words, the total metal loss through scale vaporization is simply linear in time, or

⁴In Wajszel's paper (ref. 3) this is termed W_p .

$$(W_m)_{\text{vaporization loss}} = Bt \quad (\text{A8})$$

where B is the vaporization rate constant and t is elapsed time. Now the scale weight loss is simply the weight ratio factor b/a times the left side of equation (A8), or

$$W_s = \left(\frac{b}{a}\right) Bt \quad (\text{A9})$$

Integration of product scale equation. - One form of the mass-balance equation is

$$\left[\begin{array}{c} \text{Weight of} \\ \text{scale} \end{array} \right] = \frac{b}{a} \left[\begin{array}{c} \text{Weight of} \\ \text{metal oxidized} \end{array} \right] - \left[\begin{array}{c} \text{Weight of} \\ \text{scale vaporized} \end{array} \right] \quad (\text{A10})$$

or

$$W_r = \left(\frac{b}{a}\right) W_m - W_s \quad (\text{A11})$$

The time derivative of equation (A11) is

$$\frac{dW_r}{dt} = \frac{b}{a} \frac{dW_m}{dt} - \frac{dW_s}{dt} \quad (\text{A12})$$

Substituting equations (A7) and (A9) into the right side of equation (A12) reproduces Wajszel's equation (5),

$$\frac{dW_r}{dt} = \frac{b}{a} \left(\frac{b}{a} \frac{A}{W_r} - B \right) \quad (\text{A13})$$

It is seen from equation (A13) that when the derivative vanishes, we have the maximum (steady state) scale formation, that is,

$$(W_r)_{\text{max}} = \frac{b}{a} \frac{A}{B} \quad (\text{A14})$$

which will be shown to occur from the integrated form of equation (A13) as time approaches infinity as a limit.

Equation (A13) takes the form

$$\frac{z \, dz}{B^2(A - z)} = dt \quad (\text{A15})$$

where $z = BaW_r/b$. Making a second change in the variable yields

$$u = A - z$$

$$z = A - u$$

$$dz = -du$$

Then

$$\begin{aligned} \frac{1}{B^2} \int_A^{A-z} \frac{(A - u)(-du)}{u} &= \frac{-A}{B^2} \int_A^{A-z} \frac{du}{u} + \frac{1}{B^2} \int_A^{A-z} du \\ &= \frac{1}{B^2} \left(u - A \ln u \right)_A^{A-z} \\ &= \frac{1}{B^2} \left(-z - A \ln \frac{A - z}{A} \right) \\ &= t \end{aligned}$$

This finally is rearranged to Wajszel's equation (8)

$$\frac{A}{B^2} \ln \left(\frac{A}{A - \frac{B_a W_r}{b}} \right) - \frac{a W_r}{Bb} = t \quad (\text{A16})$$

We find the exponential form of equation (A16) to be more useful in the subsequent analysis:

$$R = 1 - e^{-R-T} \quad (\text{A17})$$

where

$$\left. \begin{aligned} R &= \frac{aBW_r}{bA} \\ T &= \frac{B^2t}{A} \end{aligned} \right\} \quad \text{and} \quad (A18)$$

Integration of the metal-oxidation equation. - When the scale product equation (A11) is written with equation (A9) substituted for the vaporization term, the resulting equation

$$W_r = \frac{b}{a} (W_m - Bt) \quad (A19)$$

can at once be substituted into the right side of equation (A7) to obtain the important metal-oxidation equation

$$\frac{dW_m}{dt} = \frac{A}{W_m - Bt} \quad (A20)$$

The last expression is Wajszel's equation (3a), which, along with equation (A13) (or Wajszel's (5)), constitutes the analytical basis for the computation program of this report.

The integration of equation (A20) will now be demonstrated. First, make the transformation of the variables

$$\left. \begin{aligned} M &= \frac{W_m B}{A} \\ T &= \frac{tB^2}{A} \end{aligned} \right\} \quad (A21)$$

whereupon the new form of the differential equation becomes

$$\frac{dM}{dT} = \frac{1}{M - T} \quad (A22)$$

Further, let $M - T = 1/v$. The limits on these variables are

$$\left. \begin{array}{l} \text{for } T = 0 \left\{ \begin{array}{l} (M - T) = 0 \\ v \rightarrow \infty \end{array} \right\} \\ \text{for } T \rightarrow \infty \left\{ \begin{array}{l} (M - T) = 1 \\ v = 1 \end{array} \right\} \end{array} \right\} \quad (\text{A23})$$

The integral of equation (A22) takes the form

$$\int_{-\infty}^v \frac{-1}{v^2(v^2 - 1)} dv = \int_0^T dT \quad (\text{A24})$$

Let the integrand on the left be expanded into the partial fraction

$$\frac{-1}{v^2(v - 1)} = \frac{1}{v} + \frac{1}{v^2} - \frac{1}{v - 1} \quad (\text{A25})$$

This allows equation (A24) to be immediately integrated

$$\left[\ln v - v^{-1} - \ln(v - 1) \right]_{-\infty}^v = T \quad (\text{A26})$$

or

$$\left[\ln \frac{v}{v - 1} - \frac{1}{v} \right]_{-\infty}^v = T \quad (\text{A27})$$

And since the bracket on the left vanishes at the lower limit, we then arrive at

$$\ln \frac{v}{v - 1} - \frac{1}{v} = T \quad (\text{A28})$$

or

$$\ln \frac{1}{1 - M + T} - (M - T) = T \quad (\text{A29})$$

and finally

$$\ln (1 - M + T) = -M \quad (A30)$$

Equation (A30) is one form of the definite integral of equation (A20) in terms of the non-dimensional variables M and T .

The exponential form of equation (A30) is more useful in the computer program. So

$$M = 1 + T - \exp (-M) \quad (A31)$$

which is exactly Wajszel's integral solution (eq. (7)) in terms of M and T . Replacing the M and T variables in equation (A31) by their definitions (A21) yields

$$\frac{A}{B^2} \left[-1 + \exp \left(-\frac{BW_m}{A} \right) \right] + \frac{W_m}{B} = t \quad (A32)$$

which is Wajszel's equation (7).

Estimation of sample weight change. - It is now possible to derive an expression for calculating the predicted specific sample weight change due to oxidation of the metal. In the mass-balance equation (A1) the term for the total scale formed minus the term for scale vaporization is just the product scale weight. Thus, the mass equation may be written as

$$\left[\begin{array}{c} \text{Specific sample} \\ \text{weight change} \end{array} \right] = \left[\begin{array}{c} \text{Product scale} \\ \text{weight} \end{array} \right] - \left[\begin{array}{c} \text{Weight of} \\ \text{metal oxidized} \end{array} \right] \quad (A33)$$

or

$$\Delta W = W_r - W_m \quad (A34)$$

The terms on the right are obtained from equations (A16) and (A32), respectively.

When numerical values are given for the system parameters a , A , and B , the transcendental equations (A16) and (A32) can be solved for W_m and W_r at any time t . It is necessary to solve equations (A16) and (A32) iteratively. The calculations to achieve this are described in the next section.

Numerical Procedures for the Paralinear Equations

Dimensionless forms of the equations. - The integral solutions of the W_m and W_r variables have already been obtained in equations (A16) and (A32). The transformed, nondimensionalized variables introduced in definitions (A18) and (A21) then restated the solution equations for W_m and W_r in the nondimensional forms (A17) and (A31).

The fundamental mass-balance equation (A34) will be transformed in like manner. Multiply by the ratio of coefficients B/A

$$\frac{B \Delta W}{A} = \frac{B W_r}{A} - \frac{B W_m}{A} \quad (A35a)$$

$$\frac{B \Delta W}{A} = \frac{b}{a} \left(\frac{a}{b} \frac{B}{A} W_r \right) - \frac{B W_m}{A} \quad (A35b)$$

which is reduced to

$$N = \frac{b}{a} R - M \quad (A36)$$

In this equation the transformed, nondimensionalized specific sample weight change N is the dependent variable as a function of the scaled independent variable time T .

The phrasing of physical laws in terms of nondimensional variables, as far as possible, is a rather common practice within disciplines which use modeling techniques to cope with very complicated problems. Among these other fields are aerodynamics and hydraulics, hydrology, chemical reactor design, river and harbor studies, and analysis of smoke dispersion from stacks. The technique is known by a variety of labels: similitude, modeling and scaling, similarity analysis. In its crudest form, it is represented by the dimensional analysis used by Lord Rayleigh and Osborne Reynolds (ref. 9).

The present study has already demonstrated that a practical advantage of scaling (nondimensionalizing) arises from the simplification of the form of the model equations. It will be apparent later in the discussion of the iterative solution of equations (A17) and (A31) that the computer subprogram requires no transfer of system coefficients or parameters other than the independent variable T . Also, further insight into the implications of the basic system models results from working with the simpler forms and solutions of the scaling analysis. This will now lead to some additional and useful properties.

Properties and trends of the model. - The mathematical limits of the relations (A17), (A31), and (A36) are

$$\left. \begin{array}{l} \text{for } T = 0 \left\{ \begin{array}{l} R = 0 \\ M = 0 \\ N = 0 \end{array} \right. \\ \\ \text{for } T \gg 1 \left\{ \begin{array}{l} R \rightarrow 1 \\ M \rightarrow 1 + T \\ N \rightarrow a^{-1} - T \end{array} \right. \end{array} \right\} \quad (\text{A37})$$

Equation (A36) will be examined for an optimum point. But first note that equations (A17) and (A31) have equivalent forms if

$$M = R + T \quad (\text{A38})$$

which is actually a restatement of the mass-balance equation (A10). To search for a maximum point on the (N, T) curve, the derivative of equation (A36) is set to zero,

$$\frac{dN}{dT} = \frac{b}{a} \frac{dR}{dT} - \frac{dM}{dT} = 0 \quad (\text{A39a})$$

Then

$$\frac{b}{a} \frac{1 - \bar{R}}{\bar{R}} - \frac{1}{\bar{M} - \bar{T}} = 0 \quad (\text{A39b})$$

and

$$\frac{b}{a} \frac{1 - \bar{R}}{\bar{R}} - \frac{1}{\bar{R}} = 0 \quad (\text{A39c})$$

The terms for dR/dT and dM/dT on the right in equation (A39b) are from equations (A17) and (A31) and use has been made of equation (A38) to obtain (A39c). The special notation for \bar{R} , \bar{M} , and \bar{T} refers to those values at optimum \bar{N} .

Equation (A39c) results in

$$\bar{R} = \frac{1}{b} \quad (\text{A40})$$

The logarithmic form of equation (A17) shows time at maximum \bar{N} to be

$$\begin{aligned} \bar{T} &= -\bar{R} - \ln(1 - \bar{R}) \\ &= \ln\left(\frac{b}{a}\right) - \frac{1}{b} \end{aligned} \quad (\text{A41})$$

From equation (A38),

$$\begin{aligned}\overline{M} &= \frac{1}{b} + \ln\left(\frac{b}{a}\right) - \frac{1}{b} \\ &= \ln\left(\frac{b}{a}\right)\end{aligned}\tag{A42}$$

and for the maximum \overline{N} , from equation (A36),

$$\begin{aligned}\overline{N} &= \frac{b}{a} \left(\frac{1}{b}\right) - \ln\left(\frac{b}{a}\right) \\ &= \frac{1}{a} - \ln\left(\frac{b}{a}\right)\end{aligned}\tag{A43}$$

It is of interest to note that the values of \overline{N} , \overline{M} , \overline{R} , and \overline{T} depend only on the value of the stoichiometric coefficient a . These special values for \overline{N} and \overline{T} have been given the notation

$$\left. \begin{aligned}\alpha &= \frac{1}{a} - \ln\left(\frac{b}{a}\right) \\ \beta &= \ln\left(\frac{b}{a}\right) - \frac{1}{b}\end{aligned}\right\}\tag{A44}$$

From the definitions of T and N in equations (A18) and (A36), respectively, it can be shown that

$$\begin{aligned}N &= \overline{N} \left(\frac{\Delta W}{\overline{\Delta W}}\right) \\ &= \alpha \left(\frac{\Delta W}{\overline{\Delta W}}\right)\end{aligned}\tag{A45a}$$

and

$$\begin{aligned}T &= \overline{T} \left(\frac{t}{\overline{t}}\right) \\ &= \beta \left(\frac{t}{\overline{t}}\right)\end{aligned}\tag{A45b}$$

from which it should be noted that the scaling of N and T is based on $\Delta\bar{W}$ and \bar{t} , respectively, the maximum specific net sample weight change and the time at which it occurs.

The rate coefficients A and B reflect the values of $\Delta\bar{W}$ and \bar{t} . From the definitions of N and T (eqs. (A36) and (A18)) and the optimum values $\bar{N} = \alpha$, $\bar{T} = \beta$, there results

$$\left. \begin{aligned} A &= \frac{\beta}{\bar{t}} \left(\frac{\Delta\bar{W}}{\alpha} \right)^2 \\ B &= \frac{\beta}{\alpha} \frac{\Delta\bar{W}}{\bar{t}} \end{aligned} \right\} \quad (A46)$$

This last relation provides a most convenient method for calculating the rate coefficients from limited experimental data.

Another obvious examination point occurs at the time T_0 when $N = 0$, which is designated the "crossover point." From equation (A36) we have

$$\frac{bR_0}{a} = M_0 \quad (A47)$$

Using equation (A38), this becomes

$$R_0 = aT_0 \quad (A48a)$$

or

$$M_0 = bT_0 \quad (A48b)$$

Either of the forms of equation (A48) substituted into equation (A17) for R_0 , or into equation (A31) for M_0 leads to the equation

$$aT_0 = 1 - e^{-bT_0} \quad (A49)$$

which must be solved by an approximate technique. This also shows that T_0 is only a function of the stoichiometric coefficient. Table V illustrates the general values of these dimensionless variables over a range of values of the coefficient a .

One of the consequences of the parilinear model is obtained from the last column in table V, which shows that the ratio of crossover time to time at optimum sample weight change T_0/\bar{T} is about 4.

Table VI summarizes the results of this analytical section on the properties and trends of the model. Four time values are exhibited: initial time $t = 0$, time at maximum specimen weight gain \bar{t} , time at zero specimen weight gain t_0 , and finally very long times where the variables N , M , R , and dN/dT approach limiting values.

Table VII summarizes the definitions of the much-used parilinear parameters and their development from basic physical variables (i.e., their correspondence with the transport coefficients k_p and k_v).

Numerical solutions of the equations. - We have seen that the nature of the parilinear model is such that the history (or curve) of ΔW as a function of t is uniquely predicted from a knowledge of three constants: a , A , and B .

Conversely, two data points $(\Delta W_1, t_1)$ and $(\Delta W_2, t_2)$ can, in principle, be used to calculate the values of A and B that are needed to give the unique curve passing through those data points. This is, of course, about the only way to obtain estimates of A and B from the laboratory experiments.

This section outlines those numerical techniques for solving the parilinear equations that are the algorithms for the FORTRAN program. The complete program procedure is in the following sequence:

- (1) Establish values of the system parameters α , β , A , B , T_0
- (2) Solve the transcendental parilinear equations in dimensionless form by approximation methods
- (3) Use these solutions to obtain a group of results:
 - (a) The array of ΔW 's for a given array of t values
 - (b) The special results $W_{m,0}$, W_m , \bar{W}_r , $W_{r,\lim}$
 - (c) The times t_δ at which $W_r = \delta \cdot W_{r,\lim}$
 - (d) The times t corresponding to chosen values of W_m

System parameters. - The crossover point T_0 is obtained from equation (A49) by using successive substitutions of improved approximations to T_0 , starting with an initial value of $T_0 = 4\beta$. The convergence was rapid in satisfying the test

$$\left| \frac{T_{j+1} - T_j}{T_j} \right| < 0.0001 \quad (\text{A50})$$

The values of A and B are obtained by using one of four data input types: (1) defined values of k_p and k_v (table VI); (2) given values of $(\Delta \bar{W}, \bar{t})$ (eq. (A46)); (3) a given value of k_p or k_v and one general data pair $(\Delta W, t)$; (4) experimental data pairs $(\Delta W_1, t_1)$ and $(\Delta W_2, t_2)$. The computation using the third type differs depending on

whether k_p or k_v is defined.

Example 1 - Define k_p :

$$A = \frac{k_p a^2}{2}$$

From equations (A36) and (A38),

$$\begin{aligned} R &= a(N + T) \\ &= \frac{aB}{A} (\Delta W + Bt) \end{aligned} \quad (A51)$$

The terms in (A51) are known except for B , which makes the equation quadratic in B . Both equations (A51) and (A17) are to be satisfied. Write equation (A17) in its alternate form

$$T = \ln(1 - R) - R \quad (A17a)$$

or

$$f(B) = T + R + \ln(1 - R) \quad (A17b)$$

where $f(B) = 0$ when the correct value of B is obtained to satisfy both equations. The B-root of equation (A17b) is obtained by using the Newton-Raphson technique

$$B_{j+1} = B_j - \frac{f(B_j)}{f'(B_j)} \quad (A52)$$

where

$$\begin{aligned} f'(B_j) &= \left(\frac{df}{dB} \right)_j \\ &= \frac{\left(\frac{dT}{dB} \right)_j - R(B_j) \left(\frac{dR}{dB} \right)_j}{1 - R(B_j)} \end{aligned} \quad (A53)$$

where

$$\left(\frac{dT}{dB_j}\right) = \frac{2B_j t}{A}$$

$$\frac{dR}{dB_j} = \frac{1}{B_j} (R_j + aT_j)$$

$$R_j = \frac{aB_j}{A} (\Delta W + B_j t)$$

$$T_j = \frac{B_j^2 t}{A}$$

$$f(B_j) = T_j + R_j + \ln(1 - R_j)$$

The initial value of B_1 is obtained from the definition of T , that is,

$$B_1 = \sqrt{\frac{AT_1}{t}} \quad (A54)$$

where T_1 is arbitrarily taken at $R_1 = 0.5$, that is, half of its maximum value. Convergence of the Newton-Raphson method to the limit test is rapid:

$$\left| \frac{B_{j+1} - B_j}{B_j} \right| < 0.00001 \quad (A55)$$

Example 2 - Define k_v :

$$B = \frac{ak_v}{b} \quad (A46)$$

Equations (A51) and (A17b) are again used, but with A as the unknown coefficient. By analogy to example 1,

$$f(A_j) = T_j + R_j + \ln(1 - R_j) \quad (A56)$$

where $f(A) = 0$ at convergence. Again Newton-Raphson uses

$$A_{j+1} = A_j - \frac{f(A_j)}{f'(A_j)} \quad (\text{A57})$$

where

$$\begin{aligned} f'(A_j) &= \frac{df}{dA_j} \\ &= \frac{dT}{dA_j} - \frac{R_j}{1 - R_j} \frac{dR}{dA_j} \end{aligned}$$

and

$$\begin{aligned} \frac{dT}{dA_j} &= -\frac{T_j}{A_j} \\ \frac{dR}{dA_j} &= -\frac{R_j}{A_j} \\ f'(A_j) &= \frac{-T_j + \frac{R_j^2}{1 - R_j}}{A_j} \end{aligned} \quad (\text{A58})$$

Numerical iteration is handled as in example 1.

Example 3 - Define two experimental points, $(\Delta W_1, t_1)$ and $(\Delta W_2, t_2)$: We start with the mass-balance equation (A36) and replace R by equation (A38)

$$aN = M - bT \quad (\text{A59a})$$

$$\frac{aB}{A} \Delta W = M - bT \quad (\text{A59b})$$

For both pairs, when the weights are nonzero, we have for the two times ($t_2 > t_1$), from equation (A59b),

$$\frac{M_1 - bT_1}{\Delta W_1} = \frac{M_2 - bT_2}{\Delta W_2}$$

$$M_1 - \left(\frac{\Delta W_1}{\Delta W_2}\right)M_2 + bT_1 \left(\tau \frac{\Delta W_1}{\Delta W_2} - 1\right) = f(T_1) \quad (\text{A60})$$

where $\tau = T_2/T_1 = t_2/t_1$ and $f(T_1) = 0$ when the parameters A and B are evaluated such that T_1 and $T_2 = \tau T_1$ give M_1 and M_2 values which satisfy equation (A60).

The T_1 root of equation (A60) is found by using the Wegstein secant modification of the iteration technique for successive estimates on T_1 :

$$T_{j+1} = f(T_j)$$

$$= \frac{\frac{\Delta W_1 M_2}{\Delta W_2} - M_1}{b \left(\frac{\Delta W_1 t_2}{\Delta W_2 t_1} - 1 \right)} \quad (\text{A61})$$

where M_2 and M_1 are calculated for given τT_j and T_j , respectively, by using the Newton-Raphson iterative method to solve equation (A31):

$$M_{i+1} = M_i - \frac{F(M_i)}{F'(M_i)} \quad (\text{A62})$$

where

$$F(M_i) = -M_i + 1 + T_j - \exp(-M_i) \quad (\text{A63})$$

$$F'(M_i) = \frac{dF}{dM_i} = T_j - M_i \quad (\text{A64})$$

The Newton-Raphson method rapidly converges for given values of T_j .

A safe starting value for T_j in equation (A61) is T_0 , from (A50), and the initial $M_0 = bT_0$ in equations (A62) and (A64).

Wegstein's iteration scheme is used to get accelerated convergence in the case of a function, such as equation (A61), that has at least a continuous first derivative in the range in which the iteration moves. It refines an initial guess T_0 of the root of our nonlinear equation $T = f(T)$.

The calculation sequence starts as follows

$$x_1 = y_0 = f(x_0)$$

$$y_1 = f(x_1)$$

with the succeeding steps resulting in the computational scheme

$$\left. \begin{aligned} x_{i+1} &= x_i + \frac{x_i - x_{i-1}}{\frac{x_{i-1} - y_{i-1}}{x_i - y_i} - 1} \\ y_{i+1} &= f(x_{i+1}) \end{aligned} \right\} \quad (i = 1, 2, \dots) \quad (A65)$$

Each step requires one evaluation of $f(x)$.

The iterative procedure is terminated when the following two conditions are satisfied:

$$\text{DEL1} \leq \epsilon \quad \text{and} \quad \text{DEL2} \leq 10 \cdot \epsilon$$

with

$$\text{DEL1} = \begin{cases} \left| \frac{x_{i+1} - x_i}{x_{i+1}} \right| & \text{when } |x_{i+1}| > 1 \\ |x_{i+1} - x_i| & \text{when } |x_{i+1}| \leq 1 \end{cases}$$

$$\text{DEL2} = \begin{cases} \left| \frac{x_{i+1} - y_{i+1}}{T_{i+1}} \right| & \text{when } |x_{i+1}| > 1 \\ |x_{i+1} - y_{i+1}| & \text{when } |x_{i+1}| \leq 1 \end{cases}$$

and the tolerance factor ϵ is specified in the input.

The calculation of the parameters A and B follows after convergence of equations (A61) and (A64) to a suitable test, such as was used for equation (A54). The computed values of M_1 and T_1 are used in equation (A59) to determine

$$\frac{B}{A} = \frac{M_1 - bT_1}{a \Delta W_1} \quad (\text{A66})$$

and from equation (A18)

$$\frac{B^2}{A} = \frac{T_1}{t_1} \quad (\text{A67})$$

Dividing equation (A67) by (A66) gives the sublimation parameter

$$B = \frac{T_1}{t_1} \left(\frac{M_1 - bT_1}{a \Delta W_1} \right) \quad (\text{A68})$$

and finally the parabolic parameter A is obtained from either equation (A66) or (A67), for instance,

$$A = \frac{B^2 t_1}{T_1} \quad (\text{A69})$$

For the special case in which one given weight is zero (crossover point), the associated time is t_0 , which establishes the important \bar{t} and thus the $B^2/A = \beta/\bar{t}$. The non-zero weight-against-time pair $(\Delta W, t)$ is used to establish the time $T = (\beta/\bar{t})t$ and the associated M -value from equation (A64). Finally, from equations (A68) and (A69) the individual parameters A and B are computed.

Table VIII summarizes the four possible input types used to establish the necessary system parameters.

Main program calculation. - With numerical values of the parilinear parameters a, A, and B, the main results can be calculated by using the relations already established.

Net specimen weight curve: Given an array of LL times at which values of net specimen weight are wanted, specify t_1, t_2, \dots, t_{LL} in hours and calculate

$$T_1, T_2, \dots, T_{LL} \quad \text{from equation (A21)}$$

$$M_1, M_2, \dots, M_{LL} \quad \text{from equation (A31)}$$

$$N_1, N_2, \dots, N_{LL} \quad \text{from equation (A59a)}$$

$$\Delta W_1, \Delta W_2, \dots, \Delta W_{LL} \quad \text{from equation (A59b)}$$

$$W_{m,1}, W_{m,2}, \dots, W_{m,LL} \quad \text{from equation (A21)}$$

$$W_{r,1}, W_{r,2}, \dots, W_{r,LL} \quad \text{from equation (A18)}$$

$$\delta_{m,1}, \delta_{m,2}, \dots, \delta_{m,LL} \quad \text{from equation (A70)}$$

$$\delta_{r,1}, \delta_{r,2}, \dots, \delta_{r,LL}$$

The last two rows of thicknesses are calculated as

$$(\text{Metal thickness lost}) = \frac{W_m}{\rho_m} = \delta_m \quad (\text{A70})$$

where metal density is ρ_m , and for the thickness of the scale layer at any time

$$(\text{Scale thickness}) = \frac{W_r}{\rho_r} = \delta_r \quad (\text{A71})$$

where ρ_r is the scale density. These calculations are found in FORTRAN subroutine CURVE.

Special weight values: Table IX completes the trends and limiting values of table VI. These calculations are found in the FORTRAN subroutine SPEVAL.

Product scale thickness-against-time values: It is required to determine the experimental times for the model sample to reach certain specified fractions of the equilib-

rium (limiting) scale thickness. Given the fractions $R_1, R_2, R_3 < 1$, calculate T_1, T_2 , and T_3 from equation (A16) and t_1, t_2 , and t_3 from equation (A21). These are calculated from the FORTRAN subroutine PROVAL.

Metal corrosion-time values: Analogous to the preceding paragraph, estimate the times required for the sample to suffer corrosion losses of specified values. Thus, given LLX values ($W_{m,1}, W_{m,2}, \dots, W_{m,LLX}$), calculate M_1, M_2, \dots, M_{LLX} from equation (A21), and t_1, t_2, \dots, t_{LLX} from equation (A32). This is programmed in FORTRAN subroutine CORODE.

APPENDIX B

BASIC COREST FORTRAN PROGRAM

```
C
C
C **** PROGRAM ANALYSIS OF METAL OXIDATION/SCALE VAPORIZATION BY
C MEANS OF PARALINEAR KINETIC MODEL. REFERENCE -- D.WAJZEL,
C J.ELECTROCHEM. SOC.,VOL.110,NO.6,JUNE 1963,P6S.504-507.
C
C THE PROGRAM PROVIDES THE HISTORY OF THE NET SAMPLE WEIGHT,
C ALLOY METAL CORRODED, AND SCALE THICKNESS.
C
C **** ADDITIONAL RESULTS PROVIDED FROM THE BASIC SOLUTION ARE --
C (1)CROSSOVER TIME FOR NET SPECIMAN WEIGHT CHANGE OF ZERO
C (2)MAXIMUM NET SAMPLE WEIGHT AND ITS CORRESPONDING TIME;
C (3)WEIGHT OF METAL CORRODED UP TO CROSSOVER TIME;
C (4)EQUILIBRIUM WEIGHT OF SCALE RETAINED ON THE SAMPLE
C AT VERY LARGE TIMES;
C (5)ELAPSED TIME FOR AN EXPECTED WEIGHT LOSS OF ALLOY;
C (6)TIME TO REACH SPECIFIED FRACTIONS OF EQUILIBRIUM
C SCALE THICKNESS;
C (7)PARALINEAR PARAMETERS ARE DETERMINED FROM THE
C EXPERIMENTAL DATA IN THOSE CASES WHERE THEY ARE
C NOT GIVEN AS INITIAL INPUT.
C
C **** PROBLEM DEFINITION AND DATA DESCRIPTION CARDS ARE LISTED AS -
C CARD 1 - FLAG FOR TYPE OF SCALE LOSS. TRUE =SPALLING,
C FALSE =VAPORIZATION.
C CARD 2 - ALLOY TYPE,ALLOY DENSITY
C CARD 3 - SCALE TYPE,SCALE DENSITY.
C CARD 4 - DATA SOURCE AND RUN DESCRIPTION.
C CARD 5 - EXPERIMENTAL TEMPERATURE AND PRESSURE.
C CARD 6 - FLAG FOR MICROFILM PLOT REQUEST. TRUE = PLOTS
C WANTED, FALSE = UNWANTED.
C
C DIMENSION HOURS(100),OP(10),XXX(10),TP(10),TTT(100)
C DIMENSION WW(100),TT(100),XKP(100),XKV(100)
C DIMENSION WM(100),WR(100),WT(100),THKLOS(100),OXITHK(100)
C DIMENSION ALLOY(6),SCALE(6),SOURCE(8),RUN(2),TEMP(2),PRESS(2)
C
C REAL KP,KV
C LOGICAL SPALL,SEMILG
C
C COMMON/BLK1/HOURS,OP,XXX,WW,TT
C COMMON/BLK2/ASMALL,BSMALL,DENOX,DENMET
C COMMON/BLK3/ITYPE,LTYPE,LL,LLX,NUMSET,NUMKP,NUMKV
C COMMON/PARAM1/ALPHA,BETA/PARAM2/TAUZRO,RATIO
C COMMON/CASE1/KP,KV/CASE2/ACAP,BCAP/CASE3/WBAR,TBAR,TZERO
C COMMON/CASE4/XKP,XKV
C COMMON/VAL1/WMBAR,WRBAR,WMZERO,WRLIM
C COMMON/SCALE/TP/RUST/TTT
C COMMON/VOLUP/WM,WR,WT,THKLOS,OXITHK
C COMMON/INFO/ALLOY,SCALE,SOURCE,RUN,TEMP,PRESS
C
C ..ARRAYS FOR MICROFILM PLOTTING ROUTINE
C DIMENSION XTITLE(4),YMLEG(9),YPLEG(10),YTLEG(9)
C COMMON/TITLES/XTITLE,YMLEG,YPLEG,YTLEG
```

```

COMMON/LEGEND/XLEG(20),YLEG(20),NX,NY
COMMON/BLKPLT/KKK(10)
COMMON/FILM/SEMILG

```

```

C
CS*****
C *** INITIALIZE DATA AND STOICHIOMETRIC COEFFICIENTS ---
C
      CALL BEGIN
CS*****
C *** DESCRIPTION OF DATA TYPE ---
C
      ITYPE=1 ---- THE DATA SET CONSISTS OF THE CURVE PARA-
C                   METER PAIR WBAR,TBAR .
C
      ITYPE=2 ---- THE DATA SET CONTAINS NUMSET PAIRED VALUES
C                   OF THE PARALINEAR OXIDATION-REACTION PARA-
C                   METER KP, AND THE VAPORIZATION PARAMETER KV.
C
      ITYPE=3 ---- GIVEN NUMSET PAIRS OF EXPERIMENTAL DATA
C                   POINTS WW(I),TT(I),NUMKP VALUES OF THE PARA-
C                   LINEAR PARAMETER KP -- (LTYPE=1) OR NUMKV
C                   VALUES OF THE VAPORIZATION PARAMETER KV --
C                   (LTYPE=2) .
C
      ITYPE=4 ---- GIVEN NUMSET PAIRS OF EXPERIMENTAL WEIGHTS
C                   W1(I),W2(I) AND THEIR CORRESPONDING TIMES
C                   T1(I),T2(I) .
C
CS*****
C *** CYCLE THROUGH DATA VECTOR ---
      DO 500 I=1,NUMSET
C
C *** TEST FOR DATA TYPE ---
      GO TO (60,70,80,90),ITYPE
C
      60 CONTINUE
CS*****
C      **** ITYPE=1
      WBAR=WW(I)
      TBAR=TT(I)
      WRITE(6,40)WBAR,TBAR
      CALL QUERY1(WBAR,TBAR)
      CALL OUTPUT
      GO TO 500
C
C
      70 CONTINUE
C
CS*****
C      **** ITYPE=2
      KP=XKP(I)
      KV=XKV(I)
      WRITE(6,42)KP,KV
      CALL QUERY2(KP,KV)
      CALL OUTPUT
      GO TO 500
C
C
      80 CONTINUE
CS*****
C      **** ITYPE=3
C

```

```

      WZZ=WW(I)
      TZZ=TT(I)
C
C      *** TEST FOR INPUT TYPE OF PARALINEAR PARAMETER ***
      GO TO (810,820),LTYPE
C
      810      CONTINUE
            DO 811 JKP=1,NUMKP
                  KP=XKP(JKP)
                  WRITE(6,45)KP,WZZ,TZZ
                  CALL QUERY3(LTYPE,WZZ,TZZ,KP)
                  CALL OUTPUT
      811      CONTINUE
            GO TO 500
C
      820      CONTINUE
            DO 821 JKV=1,NUMKV
                  KV=XKV(JKV)
                  WRITE(6,46)KV,WZZ,TZZ
                  CALL QUERY3(LTYPE,WZZ,TZZ,KV)
                  CALL OUTPUT
      821      CONTINUE
            GO TO 500
C
      90 CONTINUE
C*****
C      **** ITYPE=4
C
      N4=2*I
      N4MIN1=N4-1
      W1=WW(N4MIN1)
      W2=WW(N4)
      T1=TT(N4MIN1)
      T2=TT(N4)
      WRITE(6,47)W1,T1
      WRITE(6,48)W2,T2
      CALL QUERY4(W1,W2,T1,T2)
      CALL OUTPUT
      GO TO 500
C
C
      500 CONTINUE
C
C*****
C      **** FORMAT STATEMENTS FOLLOW ****
      40 FORMAT(////10X,26HINPUT DATA----      WMAX = ,F12.6,12X,7HTMAX = ,
            1F12.6,///)
      42 FORMAT(////10X,24HINPUT DATA----      KP = ,F12.8,12X,5HKV = ,
            1F12.8,///)
      45 FORMAT(////10X,23HINPUT DATA----      KP =,F12.8,10X,7HWW(1) =,
            1F 12.6,10H MG/SO.CM.,10X,7HTT(1) =,F12.6,6H HOURS///)
      46 FORMAT(////10X,23HINPUT DATA----      KV =,F12.8,10X,7HWW(1) =,
            1F 12.6,10H MG/SO.CM.,10X,7HTT(1) =,F12.6,6H HOURS///)
      47 FORMAT(////10X,26HINPUT DATA----      WW(1) =,F12.6,15X,7HTT(1) =,
            1F12.6,6H HOURS///)
      48 FORMAT(29X,7HWW(2) =,F12.6,15X,7HTT(2) =,F12.6,6H HOURS///)
C
      STOP
      END

```



```

SUBROUTINE BEGIN
C
C **** SUBPROGRAM READS PROGRAM DESCRIPTORS FROM DATA CARDS AND
C      WRITES INITIAL HEADINGS ON OUTPUT. ****
C
LOGICAL SPALL,SEMILG
C
DIMENSION ALLOY(6),SCALE(6),SOURCE(8),RUN(2),TEMP(2),PRESS(2)
COMMON/BLK2/ASMLL,BSMLL,DENOX,DENMET
COMMON/BLK3/ITYPE,LTYPE,LL,LLX,NUMSET,NUMKV,NUMKP
COMMON/PARAM1/ALPHA,BETA/PARAM2/TAUZRO,RATIO
COMMON/INFO/ALLOY,SCALE,SOURCE,RUN,TEMP,PRESS
COMMON/FILM/SEMILG
C
READ(5,1)SPALL
READ(5,2)ALLOY,DENMET
READ(5,3)SCALE,DENOX
READ(5,4)SOURCE,RUN
READ(5,5)TEMP,PRESS
READ(5,6)SEMILG
C
      IF (SPALL)GO TO 20
      WRITE(6,100)
      GO TO 30
20    WRITE(6,200)
30    WRITE(6,300)ALLOY,SCALE
      WRITE(6,400)TEMP,PRESS
      WRITE(6,500)SOURCE,RUN
      WRITE(6,600)DENMET,DENOX
      WRITE(6,700)ASMLL,BSMLL
      WRITE(6,800)ITYPE
      WRITE(6,900)
      CALL STOICH
      CALL ZERO
      WRITE(6,950)ALPHA,BETA,RATIO
C
1    FORMAT(1L5)
2    FORMAT(6A6,F6.3)
3    FORMAT(6A6,F6.3)
4    FORMAT(8A6,2A6)
5    FORMAT(2A6,2A6)
6    FORMAT(1L5)
C
100  FORMAT(1H1,35X,62HPARALINEAR KINETICS STUDY OF CORROSION WITH SCAL
      IE VAPORIZATION//)
200  FORMAT(1H1,35X,52HPARALINEAR KINETICS STUDY OF CORROSION WITH SPAL
      ILING//)
300  FORMAT(1H0,35X,11HALLOY TYPE-,5X,6A6//35X,11HSCALE TYPE-,5X,6A6)
400  FORMAT(1H0,35X,14HTEMPERATURE = ,2A6,10X,11HPRESSURE = ,2A6)
500  FORMAT(1H0,35X,12HDATA SOURCE- ,8A6,10HRUN NO. = ,2A6)
600  FORMAT(1H0,20X,18HDENSITIES- ALLOY = ,F6.3,21H GM/CU.CM., SCALE
      1= ,F6.3,10H GM/CU.CM.)
700  FORMAT(1H0,20X,39HSTOICHIOMETRIC COEFFICIENTS- ASMLL = ,F7.4,12H
      1 , BSMLL = ,F7.4)
800  FORMAT(1H0,20X,12HDATA TYPE = ,11)
900  FORMAT(1H0,5X,19HDATA SPECIFICATION-//15X,53HITYPE=1 ---- THE DATA
      1 SET CONSISTS OF THE CURVE PARA-/28X,22HMETER PAIR WBAR,TBAR .//
      215X,54HITYPE=2 ---- THE DATA SET CONTAINS NUMKP VALUES OF THE/
      328X,43HPARALINEAR DIFFUSION-REACTION PARAMETER KP,/28X,42HAND NUMK
      4V VALUES OF THE VAPORIZATION PARA-/28X,10HMETER KV .//15X,52HITYPE

```

```

5=3 ---- GIVEN NUMSET PAIRS OF EXPERIMENTAL DATA/28X,44HPOINTS WW(I
6),TT(I),NUMKP VALUES OF THE PARA-/28X,41HLINEAR PARAMETER KP -- (L
7TYPE=1) OR NUMKV/28X,42HVALUES OF THE VAPORIZATION PARAMETER KV --
8/28X,11H(LTYPE=2) .//15X,55HITYPE=4 ---- GIVEN NUMSET PAIRS OF EXP
9ERIMENTAL WEIGHTS/28X,41HW1(I),W2(I) AND THEIR CORRESPONDING TIMES
1/28X,13HT1(I),T2(I) .//)
950 FORMAT(10X,8HALPHA = ,F10.9,12X,7HBETA = ,F10.9,13X,38HCROSSOVER T
1IME/TIME (AT MAX. WEIGHT) = ,F8.6,/)

```

C

```

RETURN
END

```

SUBROUTINE OUTPUT

C

```

DIMENSION HOURS(100),OP(10),XXX(10),TP(10),TTT(100)
DIMENSION WW(100),TT(100),XKP(100),XKV(100)
DIMENSION WM(100),WR(100),WT(100),THKLOS(100),OXITHK(100)
DIMENSION ALLOY(6),SCALE(6),SOURCE(8),RUN(2),TEMP(2),PRESS(2)

```

C

```

REAL KP,KV
LOGICAL SPALL,SEMILG

```

C

```

COMMON/BLK1/HOURS,OP,XXX,WW,TT
COMMON/BLK2/ASMALL,BSMALL,DENOX,DENMET
COMMON/BLK3/ITYPE,LTYPE,LL,LLX,NUMSET,NUMKP,NUMKV
COMMON/PARAM1/ALPHA,BETA/PARAM2/TAUZRO,RATIO
COMMON/CASE1/KP,KV/CASE2/ACAP,BCAP/CASE3/WBAR,TBAR,TZERO
COMMON/CASE4/XKP,XKV
COMMON/VAL1/WMBAR,WRBAR,WMZERO,WRLIM
COMMON/SCALE/TP/RUST/TTT
COMMON/VOLUP/WM,WR,WT,THKLOS,OXITHK
COMMON/INFO/ALLOY,SCALE,SOURCE,RUN,TEMP,PRESS

```

C

```

C.,NAMED COMMON FOR MICROFILM PLOTTING ROUTINE
DIMENSION XTITLE(4),YMLEG(9),YPLEG(10),YTLEG(9)
COMMON/TITLES/XTITLE,YMLEG,YPLEG,YTLEG
COMMON/BLKPLT/KKK(10)
COMMON/FILM/SEMILG

```

C

```

CS*****

```

C

```

C *** PRINTOUT FOR BULK OF COMPUTED RESULTS ***

```

C

```

CS*****

```

C

```

100      CALL SPEVAL
        WRITE(6,12)ACAP,BCAP,KP,KV,TZERO
        WRITE(6,13)WBAR,WRLIM
        WRITE(6,14)TBAR,WMZERO
        WRITE(6,15)WMBAR,WRBAR
        WRITE(6,16)
        CALL PROVAL
        WRITE(6,17) (OP(K),TP(K),K=1,3)
        WRITE(6,18)
        CALL CORODE

```

```

        WRITE(6,19)(XXX(II),TTT(II),II=1,LLX)
        WRITE(6,21)
        CALL CURVE
        WRITE(6,23)(HOURS(IJ),WM(IJ),WR(IJ),WT(IJ),THKLOS(IJ),
1              OXITHK(IJ),IJ=1,LL)
C
C...REQUEST FOR MICROFILM SEMILOG PLOTS
        IF(SEMIL6)CALL PLOTIO(LL)
C
12 FORMAT(//10X,4HA = ,F10.7,6X,4HB = ,F10.7,6X,5HNP = ,F10.7,5X,
15HKV = ,F10.7,5X,17HCROSSOVER TIME = ,F10.2,6H HOURS//)
13 FORMAT(10X,21HMAXIMUM NET WEIGHT = ,F10.5,10H MG/SO.CM.,23X,24HLI
1MITING SCALE WEIGHT = ,F10.5,11H MG/SO.CM.//)
14 FORMAT(10X,29HTIME AT MAXIMUM NET WEIGHT = ,F10.2,7H HOURS,14X,38
1HALLOY CORRODED UP TO CROSSOVER TIME = ,F10.4,10H MG/SO.CM.//)
15 FORMAT(10X,37HALLOY CONSUMED(AT MAX. NET WEIGHT) = ,F10.4,10H MG/S
10.CM.,3X,35HSCALE WEIGHT(AT MAX.NET WEIGHT) = ,F10.4,10H MG/SO.CM.
2//)
16 FORMAT(40X,20HFRACTION OF LIMITING,14X,12HELAPSED TIME/44X,12HSCAL
1E WEIGHT,21X,7H(HOURS)//)
17 FORMAT(48X,F6.5,22X,F10.2,/)
18 FORMAT(///42X,15HALLOY CORROSION,16X,12HELAPSED TIME/43X,11H(MG/S
10.CM.),21X,7H(HOURS)//)
19 FORMAT(45X,F7.2,24X,F10.2,/)
21 FORMAT(///13X,12HELAPSED TIME,5X,14HCORROSION LOSS,6X,12HSCALE WE
1IGHT,5X,19HNET SPECIMAN WEIGHT,4X,14HCORROSION LOSS,4X,15HSCALE TH
2ICKNESS/16X,7H(HOURS),9X,11H(MG/SO.CM.),7X,11H(MG/SO.CM.),10X,
311H(MG/SO.CM.),6X,13H(MILLIMETERS),6X,13H(MILLIMETERS)//)
23 FORMAT(15X,F10.2,7X,F12.4,7X,F12.4,9X,F12.4,14X,F8.6,10X,F8.6,/)
C
        RETURN
        END

        SUBROUTINE PLOTIO(LINK)
C ... PLOT OXIDATION-CORROSION DATA. CURVES OF ALLOY WEIGHT LOSS,
C ... SCALE PRODUCT, AND NET WEIGHT LOSS VS. TIME..
C
        DIMENSION CHART(12),CHAR1(6),CHAR2(8)
        DIMENSION XTITLE(4),YMLEG(9),YPLEG(10),YTLEG(9)
        DIMENSION ALLOY(6),SCALE(6),SOURCE(8),RUN(2),TEMP(2),PRESS(2)
C
        COMMON/BLK1/HOURS(100),OP(10),XXX(10),WM(100),TT(100)
        COMMON/VOLUP/WM(100),WR(100),WT(100),THKLOS(100),OXITHK(100)
C
        COMMON/INFO/ALLOY,SCALE,SOURCE,RUN,TEMP,PRESS
        COMMON/TITLES/XTITLE,YMLEG,YPLEG,YTLEG
        COMMON/LEGEND/XLEG(20),YLEG(20),NX,NY
        COMMON/BLKPLT/KKK(10)
C
C ... LOAD LEGEND ARRAYS FROM COMMON BLOCK INPUT
        DO 10 I=1,8
            CHAR2(I)=SOURCE(I)
                J=I+6
                K=I+2

```

```

        L=I+4
        IF(I.GT.2) GO TO 5
        CHAR1(I)=TEMP(I)
        CHAR1(K)=PRESS(I)
        CHAR1(L)=RUN(I)
5       IF(I.GT.6) GO TO 10
        CHART(I)=ALLOY(I)
        CHART(J)=SCALE(I)
10      CONTINUE
C
C..OVERWRITE KKK(6) BY SUBROUTINE CALLING ARGUMENT
      KKK(6)=LINK
C
C..ABSCISSA TITLE ARRAY
      DO 20 IX=1,4
        XLEG(IX)=XTITLE(IX)
20      CONTINUE
      NX=19
C
C..SEMILOG PLOT OF ALLOY CORROSION HISTORY
      DO 30 IM=1,9
        YLEG(IM)=YMLEG(IM)
30      CONTINUE
      NY=52
      CALL LRTLEG(CHART,72)
      CALL LRLEGN(CHAR1,36,0,1.,7.,0.)
      CALL LRLEGN(CHAR2,48,0,1.,6.5,0.)
      CALL LOGXY(HOURS,WM,2,KKK)
C
C..SEMILOG PLOT OF PRODUCT SCALE HISTORY
      DO 40 IP=1,10
        YLEG(IP)=YPLEG(IP)
40      CONTINUE
      NY=60
      CALL LRTLEG(CHART,72)
      CALL LRLEGN(CHAR1,36,0,1.,7.,0.)
      CALL LRLEGN(CHAR2,48,0,1.,6.5,0.)
      CALL LOGXY(HOURS,WR,2,KKK)
C
C..SEMILOG PLOT OF NET SAMPLE WEIGHT HISTORY
      DO 50 IT=1,9
        YLEG(IT)=YTLEG(IT)
50      CONTINUE
      NY=50
      CALL LRTLEG(CHART,72)
      CALL LRLEGN(CHAR1,36,0,1.,7.,0.)
      CALL LRLEGN(CHAR2,48,0,1.,6.5,0.)
      CALL LOGXY(HOURS,WT,2,KKK)
      RETURN
      END

```

```

SUBROUTINE STOICH
COMMON/BLK2/ASMLL,BSMALL,DENOX,DENMET
COMMON/PARAM1/ALPHA,BETA

```

```

C
C*****
C
C *** FUNCTIONS OF THE STOICHIOMETRIC COEFFICIENT ASMALL ***
C      ALPHA - DIMENSIONLESS MAXIMUM NET SAMPLE WEIGHT
C      BETA - DIMENSIONLESS TIME AT NET SAMPLE WEIGHT ALPHA
C
C*****
C
C      U=BSMALL/ ASMALL
C      XL=ALOG(U)
C      ALPHA=U-1.-XL
C      BETA=XL-(1./BSMALL)
C      RETURN
C
C      END

      SUBROUTINE ZERO
C
C      COMMON/BLK2/ASMALL,BSMALL,DENOX,DENMET
C      COMMON/PARAM1/ALPHA,BETA/PARAM2/TAUZRO,RATIO
C
C*****
C
C *** FUNCTIONS OF THE STOICHIOMETRIC COEFFICIENT ASMALL ***
C      TAUZRO - PREDICTED DIMENSIONLESS TIME(FROM PARALINEAR
C              THEORY) AT CROSSOVER POINT FOR SAMPLE WEIGHT
C      RATIO - CROSSOVER TIME TO TIME AT MAXIMUM SAMPLE WEIGHT
C
C*****
C
C      1 FORMAT(1H0,20X,41HERROR ALERT MESSAGE FROM SUBROUTINE ZERO /1H ,
C              125X,67H**THE NUMBER OF ITERATIONS EXCEED 100 AND EXITS WITH THESE
C              2VALUES**)
C      2 FORMAT(1H ,30X,16HTAUZRO*ASMALL = ,F9.5/1H ,30X,37HTHE TRIAL ITERA
C              1TION VALUE **TEST** = ,F9.5//)
C
C
C      **INITIALIZE FOR FIRST ITERATION **
C      U=BSMALL/ASMALL
C      FIRST=1./BSMALL
C      PJ=SQRT(FIRST)
C
C      ** ITERATE ON NEXT ESTIMATE **
C      DO 55 I=1,100
C          DELTA=1.-PJ
C          PJJ=PJ+(ALOG(DELTA)+U*PJ)/(1./DELTA-U)
C          ZFF=(PJJ-PJ)/PJJ
C          TEST=ABS(ZFF)
C          IF(TEST.LT..00001) GO TO 105
C          PJ=PJJ
C
C      55  CONTINUE
C          WRITE(6,1)
C          WRITE(6,2)PJJ,TEST

```

```

C
105      TAUZRO=PJJ/ASMLL
        RATIO=TAUZRO/BETA
        RETURN
C
      END

```

```

      SUBROUTINE QUERY1(W,T)
      REAL KP,KV
      COMMON/BLK3/ITYPE,LTYPE,LL,LLX,NUMSET,NUMKP,NUMKV
      COMMON/BLK2/ASMLL,BSMLL,DENOX,DENMET
      COMMON/PARAM1/ALPHA,BETA/PARAM2/TAUZRO,RATIO
      COMMON/CASE1/KP,KV/CASE2/ACAP,BCAP/CASE3/WBAR,TBAR,TZERO
C
CS*****
C
C *** SUBROUTINE DETERMINES NUMERICAL VALUES OF THE PARALINEAR PARAMETERS
C       FROM ONE OF SEVERAL POSSIBLE TYPES OF INPUT DATA **
C
C *** INPUT ARGUMENTS ---- WBAR,TBAR FOR ITYPE = 1 ***
C
CS*****
C
      40 WBAR=W
        TBAR=T
C
        BCAP=WBAR*BETA/(TBAR*ALPHA)
        ACAP=BCAP*WBAR/ALPHA
        AA=ACAP/BCAP
        KP=2.*ACAP/ASMLL**2
        KV=BCAP*BSMLL/ASMLL
        TZERO=RATIO*TBAR
        RETURN
C
      END

```

```

      SUBROUTINE QUERY2(P,V)
      REAL KP,KV
      COMMON/CASE1/KP,KV/CASE2/ACAP,BCAP/CASE3/WBAR,TBAR,TZERO
      COMMON/PARAM1/ALPHA,BETA/PARAM2/TAUZRO,RATIO
      COMMON/BLK2/ASMLL,BSMLL,DENOX,DENMET
      COMMON/BLK3/ITYPE,LTYPE,LL,LLX,NUMSET,NUMKP,NUMKV
C
CS*****
C
C *** SUBROUTINE DETERMINES NUMERICAL VALUES OF THE PARALINEAR PARAMETERS
C       FROM ONE OF SEVERAL POSSIBLE TYPES OF INPUT DATA **
C
C *** INPUT ARGUMENTS ---- KP AND KV FOR ITYPE = 2 ***
C

```

```

C *****
C
60 KP=P
KV=V
C
ACAP=KP*ASMALL**2/2.
BCAP=KV*ASMALL/BSMALL
AA=ACAP/BCAP
WBAR=AA*ALPHA
TBAR=AA*BETA/BCAP
TZERO=RATIO*TBAR
RETURN
C
END

SUBROUTINE QUERY3(W,T,X)
REAL KP,KV
COMMON/BLK2/ASMALL,BSMALL,DENOX,DENMET
COMMON/BLK3/ITYPE,LTYPE,LL,LLX,NUMSET,NUMKP,NUMKV
COMMON/PARAM1/ALPHA,BETA/PARAM2/TAUZRO,RATIO
COMMON/CASE1/KP,KV/CASE2/ACAP,BCAP/CASE3/WBAR,TBAR,TZERO
C
C *****
C
C *** SUBROUTINE DETERMINES NUMERICAL VALUES OF THE PARALINEAR PARAMETERS
C FROM ONE OF SEVERAL POSSIBLE TYPES OF INPUT DATA **
C
C *** INPUT ARGUMENTS ---- ONE WEIGHT-TIME DATA PAIR PLUS EITHER KP
C OR KV FOR ITYPE = 3 **
C
C *****
C
1 FORMAT(1H0,20X,43HERROR ALERT MESSAGE FROM SUBROUTINE QUERY3 /1H ,
125X,67H**THE NUMBER OF ITERATIONS EXCEED 100 AND EXITS WITH THESE
2VALUES**/)
2 FORMAT(1H ,30X,25HTHE PARAMETER **BCAP** = ,E8.4/1H ,30X,37HTHE TR
1IAL ITERATION VALUE **TEST** = ,F9.5///)
3 FORMAT(1H ,30X,27HTHE ABSCISSA TERM **TM** = ,E8.4/1H ,30X,37HTHE
1TRIAL ITERATION VALUE **TEST** = ,F9.5///)
C
4 WW1=W
5 TT1=T
IF(LTYPE .EQ. 2) GO TO 10
C
** COEFFICIENT KP GIVEN **
KP=X
ACAP=KP*ASMALL**2/2.
C
AA=ACAP/ASMALL
BMAX=(-WW1+SQRT(WW1**2+4.*TT1/ASMALL))/2.*TT1
C
** FIRST GUESS OF BCAP VALUE **
6 B1=BMAX
C

```

```

      DO 8 J=1,100
        T1=TT1*B1**2/ACAP
        P=RETRNO(T1)-T1
        PP=(1.-P)*2.*T1/(P*B1)
        F=TT1*B1**2+WW1*B1-AA*P
        DF=2.*TT1*B1+WW1-AA*PP
        B2=B1-F/DF
        TEST=ABS((B2-B1)/B2)
        IF(TEST.LT..0001) GO TO 9
        B1=B2
8      CONTINUE
      WRITE(6,1)
      WRITE(6,2)B2,TEST
9      BCAP=B2
C
      KV=BSMALL*BCAP/ASMALL
      WBAR=ACAP*ALPHA/BCAP
      TBAR=WBAR*BETA/(BCAP*ALPHA)
      TZERO=TAUZRO*TBAR/BETA
      RETURN
C
C      **COEFFICIENT KV GIVEN **
10     KV=X
      BCAP=KV*ASMALL/BSMALL
C
C      ** ITERATION USING MODIFIED SECANT METHOD **
      CONST=BSMALL+ASMALL*WW1/(TT1*BCAP)
      TR=1./(CONST-1.)
      YR=EXP(-CONST*TR)
      TL=1./CONST
C
      DO 16 I=1,100
        EL=CONST*TL
        YL=EXP(-EL)
C
C      ** CALCULATE CHORD SLOPE **
        CS=(YR-YL)/(TR-TL)
C
C      ** ESTIMATE MEAN ABSCISSA VALUE **
        TM=(1.-YL+CS*TL)/(CONST+CS-1.)
        TEST=ABS(TM-TL)
        IF(TEST.LT..0001) GO TO 17
        TL=TM
16     CONTINUE
      WRITE(6,1)
      WRITE(6,3)TM,TEST
C
17     ACAP=TT1*BCAP**2/TM
      KP=2.*ACAP/ASMALL**2
      WBAR=ACAP*ALPHA/BCAP
      TBAR=WBAR*BETA/(BCAP*ALPHA)
      TZERO=TAUZRO*TBAR/BETA
      RETURN
C
      END

```



```

SUBROUTINE QUERY4(W1,W2,T1,T2)
REAL KP,KV
COMMON/BLK2/ASMLL,BSMLL,DENOX,DENMET
COMMON/BLK3/ITYPE,LTYPE,LL,LLX,NUMSET,NUMKP,NUMKV
COMMON/PARAM1/ALPHA,BETA/PARAM2/TAUZRO,RATIO
COMMON/CASE1/KP,KV/CASE2/ACAP,BCAP/CASE3/WBAR,TBAR,TZERO
C
CS*****
C
C *** SUBROUTINE DETERMINES NUMERICAL VALUES OF THE PARALINEAR PARAMETERS
C      FROM ONE OF SEVERAL POSSIBLE TYPES OF INPUT DATA **
C
C *** INPUT ARGUMENTS ---- TWO PAIRS OF EXPERIMENTAL WEIGHT-TIME DATA
C      FOR ITYPE = 4 **
C
CS*****
C
1  FORMAT(1H0,20X,43HERROR ALERT MESSAGE FROM SUBROUTINE QUERY4 /1H ,
125X,67H*THE NUMBER OF ITERATIONS EXCEED 200 AND EXITS WITH THESE
2VALUES**/)
2  FORMAT(1H ,30X,27HTHE ABSCISSA TERM **X2** = ,E8.4/1H ,30X,37HTHE
1TRIAL ITERATION VALUE **TEST** = ,F9.5///)
3  FORMAT(1H0,20X,43HERROR ALERT MESSAGE FROM SUBROUTINE QUERY4 /1H ,
125X,69H**DIVISOR IN ITERATION STEP IS ZERO. ERROR RETURN WITH THES
2E VALUES**/)
4  FORMAT(1H0,20X,43HERROR ALERT MESSAGE FROM SUBROUTINE QUERY4 /1H ,
125X,60H**PARAMETER C3 IS TOO SMALL. CHOOSE DIFFERENT WEIGHT PAIRS*
2**/)
C
  WW1=W1
  WW2=W2
C
  W1ABS=ABS(W1)
  W2ABS=ABS(W2)
C
  ** TEST FIRST WEIGHT FOR CROSSOVER VALUE **
  IF(W1ABS.LT..0001)GO TO 1001
C
  ** TEST SECOND WEIGHT FOR CROSSOVER VALUE **
  IF(W2ABS.LT..0001)GO TO 1002
  GO TO 80
C
  ** FIRST WEIGHT AS CROSSOVER VALUE **
1001  TZERO=T1
      TBAR=BETA*TZERO/TAUZRO
      TAU2=BETA*T2/TBAR
      EM2=RETRNO(TAU2)
      EN2=(EM2-BSMLL*TAU2)/ASMLL
      WBAR=ALPHA*W2/EN2
      GO TO 112
C
  ** SECOND WEIGHT AS CROSSOVER VALUE **
1002  TZERO=T2
      TBAR=BETA*TZERO/TAUZRO
      TAU1=BETA*T1/TBAR
      EM1=RETRNO(TAU1)
      EN1=(EM1-BSMLL*TAU1)/ASMLL
      WBAR=ALPHA*W1/EN1
      GO TO 112

```

```

C
C      ** ROUTINE FOR BOTH WEIGHT DATA NONZERO **
C
80 IEND=200                                @MAX NUMBER OF ITERATIONS
EPS=1.E-7                                @TOLERANCE BETWEEN ITERATES
IER=0                                    @ERROR CODE  ,,NO ERROR,,
      TT1=T1
      TT2=T2
      TRAT=TT2/TT1
      C1=W1/W2
      C2=TRAT*C1
      C3=BSMALL*(C2-1.)
C
      IF(ABS(C3).GT..0001)GO TO 90          @TEST ON CHOICE OF DATA
      WRITE(6,4)                          @ERROR MESSAGE
      RETURN
C
C
C..PREPARE ITERATION ON WEBSTEIN SECANT METHOD.
C
90 XSTART=TAUZRO                          @INITIAL GUESS FOR ROOT VALUE
X2=XSTART
X0=X2/TRAT
EM1=RETRNO(X0)
EM2=RETRNO(X2)
X=(C1*EM2-EM1)/C3                        @IMPLICIT RELATION X=F(X)
A=X-X0
B=-A
X0=X
X2=X0*TRAT
EM1=RETRNO(X0)
EM2=RETRNO(X2)
TEST=X-(C1*EM2-EM1)/C3
C
C
C..START ITERATION LOOP
DO 106 I=1,IEND
  IF(TEST)101,111,101
C
C..EQUATION IS NOT SATISFIED BY X
101 B=B/TEST-1.
  IF(B)102,114,102
C
C..ITERATION IS POSSIBLE
102 A=A/B                                @SECANT CORRECTION TERM
  X=X+A
  B=TEST
  X0=X
  X2=X0*TRAT
  EM1=RETRNO(X0)
  EM2=RETRNO(X2)
  TEST=X-(C1*EM2-EM1)/C3
C
C..TEST ON SATISFACTORY ACCURACY
TOL=EPS
D=ABS(X)
IF(D-1.)104,104,103
103 TOL=TOL*D
104 IF(ABS(A)-TOL)105,105,106            @FIRST TOLERANCE TEST
105 IF(ABS(TEST)-10.*TOL)111,111,106    @SECOND TOLERANCE TEST

```

```

106 CONTINUE
C..END OF ITERATION LOOP
C
      WRITE(6,1)
      WRITE(6,2)X2,TEST
      IER=1
      RETURN
C
C
C      ** CALCULATE WBAR AND TBAR FIRST **
111      TBAR=BETA*TT2/X2
      EN2=(EM2-BSMALL*X2)/ASHALL
      WBAR=ALPHA*WM2/EN2
C
112      BCAP=WBAR*BETA/(TBAR*ALPHA)
      ACAP=WBAR*BCAP/ALPHA
      KP=2.*ACAP/ASHALL**2
      KV=BSMALL*BCAP/ASHALL
      TZERO=TAUZRO*TBAR/BETA
      RETURN
C
114      IER=2
      WRITE(6,3)
      WRITE(6,2)X2,TEST
      RETURN
C
      END

```

```

SUBROUTINE SPEVAL
COMMON/BLK2/ASHALL,BSMALL,DENOX,DENMET/PARAM2/TAUZRO,RATIO
COMMON/CASE2/ACAP,BCAP/VAL1/WMBAR,WRBAR,WMZERO,WRLIM
C
C*****
C
C *** CALCULATES PHYSICAL WEIGHTS AT SPECIAL TIMES OF INTEREST --
C      1.ALLOY CORRODED AT MAXIMUM NET SPECIMAN WEIGHT, AND WHEN NET
C      GAIN IS ZERO(THAT IS,THE ZERO CROSSOVER TIME)
C      2.LIMITING SCALE WEIGHT AT INFINITE TIME, AND AT MAXIMUM NET
C      WEIGHT.
C*****
C
C
C      ** INITIALIZE RATIOS OF SYSTEM PARAMETERS **
C      U= BSMALL/ASHALL
C      AA= ACAP/BCAP
C
C      **RETURN DIMENSIONAL(PHYSICAL) WEIGHTS AT SPECIAL CONDITIONS
C      WMZERO= BSMALL*AA*TAUZRO
C      WMBAR= AA*ALOG(U)
C      WRBAR= AA/ASHALL
C      WRLIM= U*AA
C      RETURN
C
      END

```

```

SUBROUTINE CORODE
DIMENSION HOURS(100),QP(10),TP(10),XXX(100),TTT(100)
DIMENSION WM(100),TT(100)
COMMON/BLK1/HOURS,QP,XXX,WM,TT/SCALE/TP
COMMON/BLK3/ITYPE,LTYPE,LL,LLX,NUMSET,NUMKP,NUMKV
COMMON/PARAM1/ALPHA,BETA/CASE3/WBAR,TBAR,TZERO/RUST/TTT

```

```

C
CS*****
C
C *** SUBROUTINE COMPUTES ELAPSED TIME TTT WHEN XXX MILLIGRAMS PER
C      SQUARE CENTIMETER OF ALLOY HAVE BEEN CONSUMED DUE TO
C      CORROSION ***
C
CS*****
C
C      ** BEGIN LOOP THROUGH INPUT SEQUENCE OF WEIGHT LOSSES **
C      DO 5 I=1,LLX
C
C          ** TRANSFORM REAL WEIGHT TO DIMENSIONLESS VARIABLE
C          WMXXX, THEN DETERMINE CORRESPONDING DIMENSIONLESS
C          TIME TAUXXX, AND TRANSFORM IT BACK TO REAL
C          TIME TTT **
C          WMXXX=ALPHA*XXX(I)/WBAR
C          TAUXXX=RETRNT(WMXXX)
C          TTT(I)=TAUXXX*TBAR/BETA
C
5      CONTINUE
C      RETURN
C
C      END

```

```

SUBROUTINE CURVE
DIMENSION HOURS(100),QP(10),TP(10),XXX(100),TTT(100),WM(100)
DIMENSION WM(100),TT(100),WT(100),WR(100),THKLOS(100),OXITHK(100)
COMMON/BLK1/HOURS,QP,XXX,WM,TT/SCALE/TP/RUST/TTT
COMMON/BLK2/ASMALL,BSMALL,DENOX,DENMET
COMMON/BLK3/ITYPE,LTYPE,LL,LLX,NUMSET,NUMKP,NUMKV
COMMON/VOLUP/WM,WR,WT,THKLOS,OXITHK/CASE2/ACAP,BCAP

```

```

C
CS*****
C
C *** THE PRINCIPAL SUBPROGRAM WHICH COMPUTES THE NET-WEIGHT, TIME
C      PAIRS OF DATA WHICH APPROXIMATES THE EXPERIMENTAL
C      CURVE ACCORDING TO THE PARALINEAR THEORY. AT EACH
C      SPECIFIED TIME THE PROGRAM CALCULATES
C          1. NET SPECIMAN WEIGHT
C          2. METAL WEIGHT CONSUMED
C          3. WEIGHT OF SCALE FORMED
C          4. LOSS IN METAL THICKNESS
C          5. THICKNESS OF SCALE LAYER
C
CS*****
C
C

```

```

C      ** INITIALIZE THE PARALINEAR COEFFICIENTS **
C      AA=ACAP/BCAP
C
C      ** SOLVE DIMENSIONLESS OM-EQUATION AT LL TIMES
C      DO 500 J=1,LL
C          TAU=HOURS(J)*BCAP/AA
C          OM= RETRNO(TAU)
C
C          ** THREE VECTORS STORE PHYSICAL WEIGHTS OF ALLOY CORRODED,
C          SCALE FORMED, AND NET SPECIMAN WEIGHT **
C          WM(J)=OM*AA
C          WR(J)=AA*BSMALL*(OM-TAU)/ASMALL
C          WT(J)=WR(J)-WM(J)
C
C          ** TWO VECTORS STORE PHYSICAL DEPTHS OF ALLOY CORROSION
C          AND SCALE FORMED **
C          THKLOS(J)=.01*WM(J)/DENMET
C          OXITHK(J)=.01*WR(J)/DENOX
C
C      500      CONTINUE
C              RETURN
C
C      END

```

```

      FUNCTION RETRNO(TAU)
C
C*****
C
C *** SUBPROGRAM RETURNS VALUE OF DIMENSIONLESS ALLOY-CORROSION VARIABLE
C      OM AT TIME TAU **
C
C*****
C
C      1 FORMAT(1H0,20X,43HERROR ALERT MESSAGE FROM SUBROUTINE RETRNO /1H ,
C      125X,67H**THE NUMBER OF ITERATIONS EXCEED 100 AND EXITS WITH THESE
C      2VALUES**/)
C      2 FORMAT(1H ,30X,34HTHE ALLOY CORROSION TERM **OM** = ,F9.5/1H ,30X,
C      137HTHE TRIAL ITERATION VALUE **TEST** = ,F9.5//)
C
C..TEST FOR SMALL VALUES OF DIMENSIONLESS TIME..
C      X=TAU
C      IF(X.GT..01)GO TO 10
C
C..THIS SECTION USES THE NEWTON-RAPHSON METHOD FOR ROOT SOLUTION OF A
C..TRUNCATED POWER SERIES APPROXIMATION OF THE EXPONENTIAL AT VERY SMALL
C..TIMES...
C
C..FIRST GUESS AT ROOT POSITION
C      PHI=2.
C      DO 3 LLR=1,100
C          PHIX=PHI*X
C          FUNC=1.-(.5-SORT(PHIX)/6.+PHIX/24.)*PHI
C
C
C..NEWTON-RAPHSON
C      DFUNC=-.5+.25*SORT(PHIX)-PHIX/12.
C      DELPHI=-FUNC/DFUNC
C      TEST=ABS(DELPHI/PHI)
C      IF(TEST.LT..000001)GO TO 5

```

```

        PHI=PHI+DELPHI
3  CONTINUE
    WRITE(6,1)
    Y2=SQR( PHIX)
    WRITE(6,2) Y2,TEST
5  RETRNO=SQR( PHIX)
    RETURN
C    ** THIS SECTION USES NEWTON-RAPHSON TO SOLVE COMPLETE PARALINEAR
C    EQUATION FOR DIMENSINLESS CORROSION WEIGHT ..
C
C    ** SET UPPER BOUND ON THE DEPENDENT VARIABLE
10 C=1.+TAU
C
C    ** INITIALIZE FOR FIRST ITERATION **
    Y1= C
C
C    ** BEGIN NEWTONS METHOD**
    DO 13 J=1,100
        PHI= Y1+EXP(-Y1)-C
        TEST = ABS(PHI)
        IF( TEST.LT..00001) GO TO 14
11        DPHI= 1.-EXP(-Y1)
12        Y2 = Y1 - PHI/DPHI
        Y1= Y2
13    CONTINUE
        WRITE(6,1)
        WRITE(6,2) Y2,TEST
C
14    RETRNO= Y1
    RETURN
C
    END

```

```

        FUNCTION RETRNT(X)
C
C*****
C
C *** SUBPROGRAM EXPLICITLY COMPUTES DIMENSIONLESS TIME FROM THE
C      OM EQUATION ***
C
C*****
C
    RETRNT=(X-1.)+EXP(-X)
    RETURN
    END

```

APPENDIX C

KEY FORTRAN SYMBOLS FOR COREST

ACAP	parabolic scaling constant, A, in terms of W_m
ALPHA	dimensionless maximum net specific sample weight
ASMALL	stoichiometric constant, a
BCAP	linear-vaporization constant, B, in terms of W_m
BETA	dimensionless time at net specific sample weight ALPHA
BSMALL	stoichiometric constant, b
DENMET	density of the metal consumed, ρ_m
DENOX	density of the retained oxide, ρ_r
KP	parabolic scaling constant, k_p
KV	linear vaporization constant, k_v
NUMKP	number of k_p -values in input array XKP
NUMKV	number of k_v -values in input array XKV
NUMSET	number of cases in a COREST run
OXITHK	computed oxide thickness, mm
RATIO	ratio of crossover time to \bar{t} , t_0/\bar{t}
TAU	dimensionless time, B^2t/A
TAUZRO	computed dimensionless crossover time
TBAR	time to reach maximum specific sample weight change, \bar{t} , hr
THKLOS	computed metal loss, mm
WBAR	maximum specific sample weight change, $\Delta\bar{W}$
WRLIM	limiting retained specific scale weight
WRMAX	corresponding retained specific scale weight at $\Delta\bar{W}$
XKP	input array of k_p -values for data types 1, 2, and 3
XKV	input array of k_v -values for data types 1, 2, and 3

APPENDIX D

TYPICAL OUTPUT LISTING FOR COREST

BLCK DATA

```

C
C..DATA AND ARRAYS FOR PLOTTING SUBROUTINE PLOTIO(LL)
  DIMENSION XTITLE(4),YMLEG(9),YPLEG(10),YTLEG(9)
  COMMON/TITLES/XTITLE,YMLEG,YPLEG,YTLEG
  COMMON/BLKPLT/KKK(10)
  DATA KKK/3,-1,1,0,0,1,4*0/
  DATA XTITLE/19EXPOSURE TIME,HOURS/
  DATA YMLEG/52HWEIGHT OF CORRODED ALLOY,MLGMS PER SQUARE CENTIMETER
1/
  DATA YPLEG/60HWEIGHT OF ADHERING PRODUCT SCALE,MLGMS PER SQUARE CE
INTIMETER/
  DATA YTLEG/50HNET SAMPLE WEIGHT GAIN,MLGMS PER SQUARE CENTIMETER/
C
C
C..ARRAYS AND DATA FOR PROBLEM SOLUTION
  DIMENSION HOURS(100),QP(10),XXX(10),TTT(100)
  DIMENSION WW(100),TT(100),XKP(100),XKV(100)
C
  COMMON/BLK1/HOURS,QP,XXX,WW,TT/RUST/TTT
  COMMON/BLK2/ASMALL,BSMALL,DENOX,DENMET
  COMMON/BLK3/ITYPE,LTYPE,LL,LLX,NUMSET,NUMKV,NUMKP
  COMMON/CASE4/XKP,XKV
C
  INPUT FOLLOWS
C
  DATA ASMALL,BSMALL/2.1667,3.1667/
  DATA ITYPE,LL,LLX/4,17,3/
  DATA NUMSET/2/
  DATA QP/.5,.9,.95,7*0.0/
  DATA XXX/71.9,359.5,719.0,7*0.0/
  DATA HOURS/.31,.69,.86,1.11,1.64,3.06,5.83,20.83,23.61,30.56,
* 55.56,86.11,116.67,166.67,194.44,222.22,236.11,83*100./
  DATA WW/2.50,3.29,3.24,3.13,96*0.0/
  DATA TT/30.56,86.11,221.22,236.11,96*100./
C
  END

```


PARALINEAR KINETICS STUDY OF CORROSION WITH SCALE VAPORIZATION

ALLOY TYPE- CHROMIUM OXIDE FORMERS 2 SETS
 SCALE TYPE- CR2O3 TO CR03
 TEMPERATURE = 1200 C PRESSURE = 1 ATM.
 DATA SOURCE- CR-.2Y TEDMON (REF.4) BEFORE & AFTER WBAR RUN NO. =
 DENSITIES- ALLOY = 7.190 GM/CU.CH., SCALE = 5.210 GM/CU.CH.
 STOICHIOMETRIC COEFFICIENTS- ASMALL = 2.1667 , BSMALL = 3.1667
 DATA TYPE = 4

DATA SPECIFICATION-

ITYPE=1 ---- THE DATA SET CONSISTS OF THE CURVE PARAMETER PAIR WBAR,TBAR .
 ITYPE=2 ---- THE DATA SET CONTAINS NUMKP VALUES OF THE PARALINEAR DIFFUSION-REACTION PARAMETER KP, AND NUMKV VALUES OF THE VAPORIZATION PARAMETER KV .
 ITYPE=3 ---- GIVEN NUMSET PAIRS OF EXPERIMENTAL DATA POINTS WW(I),TT(I),NUMKP VALUES OF THE PARALINEAR PARAMETER KP -- (ITYPE=1) OR NUMKV VALUES OF THE VAPORIZATION PARAMETER KV -- (ITYPE=2) .
 ITYPE=4 ---- GIVEN NUMSET PAIRS OF EXPERIMENTAL WEIGHTS W1(I),W2(I) AND THEIR CORRESPONDING TIMES T1(I),T2(I) .

ALPHA = .082046594 BETA = .063698616 CROSSOVER TIME/TIME (AT MAX. WEIGHT) = 4.034745

INPUT DATA---- WW(1) = 2.500000 TT(1) = 30.560000 HOURS
 WW(2) = 3.290000 TT(2) = 86.110000 HOURS

A = .8367918 B = .0201046 KP = .3564921 KV = .0293835 CROSSOVER TIME = 532.07 HOURS

MAXIMUM NET WEIGHT = 3.41493 MG/SQ.CM.

LIMITING SCALE WEIGHT = 60.83168 MG/SQ.CM./

TIME AT MAXIMUM NET WEIGHT = 131.87 HOURS

ALLOY CORRODED UP TO CROSSOVER TIME = 33.8746 MG/SQ.CM.

ALLOY CONSUMED (AT MAX. NET WEIGHT) = 15.7949 MG/SQ.CM. SCALE WEIGHT (AT MAX. NET WEIGHT) = 19.2098 MG/SQ.CM.

FRACTION OF LIMITING
SCALE WEIGHT

ELAPSED TIME
(HOURS)

.50000	399.87
.90000	2903.72
.95000	4235.21

ALLOY CORROSION
(MG/SQ.CM.)

ELAPSED TIME
(HOURS)

71.90	1873.99
359.50	15811.57
719.00	33692.67

ELAPSED TIME (HOURS)	CORROSION LOSS (MG/SQ.CM.)	SCALE WEIGHT (MG/SQ.CM.)	NET SPECIMAN WEIGHT (MG/SQ.CM.)	CORROSION LOSS (MILLIMETERS)	SCALE THICKNESS (MILLIMETERS)
.31	.7224	1.0467	.3243	.001005	.002009
.69	1.0792	1.5571	.4778	.001501	.002989
.86	1.2055	1.7366	.5311	.001677	.003333
1.11	1.3704	1.9703	.5999	.001906	.003782
1.64	1.6678	2.3893	.7215	.002320	.004586
3.06	2.2837	3.2478	.9641	.003176	.006234
5.83	3.1632	4.4518	1.2886	.004399	.008545
20.83	6.0473	8.2263	2.1790	.008411	.015789

23.61	6.4483	8.7306	2.2823	.008968	.016757
30.56	7.3624	9.8624	2.5000	.010240	.018930
55.56	10.0308	13.0278	2.9970	.013951	.025005
86.11	12.6107	15.9007	3.2900	.017539	.030519
116.67	14.8011	18.2040	3.4030	.020586	.034941
166.67	17.8971	21.2598	3.3627	.024892	.040806
194.44	19.4419	22.7016	3.2597	.027040	.043573
222.22	20.8963	24.0110	3.1147	.029063	.046086
236.11	21.5949	24.6238	3.0290	.030035	.047263

INPUT DATA---- WW(1) = 3.240000 TT(1) = 221.219999 HOURS

 WW(2) = 3.130000 TT(2) = 236.110001 HOURS

A = .9907335 B = .0224244 KP = .4220747 KV = .0327739 CROSSOVER TIME = 506.36 HOURS

MAXIMUM NET WEIGHT = 3.62491 MG/SQ.CH. LI HITING SCALE WEIGHT = 64.57212 MG/SQ.CH./

TIME AT MAXIMUM NET WEIGHT □ 125.50 HOURS ALLOY CORRODED UP TO CROSSOVER TIME □ 35.9575 MG/SQ.CH.

ALLOY CONSUMED(AT MAX. NET WEIGHT) = 16.7661 MG/SQ.CH. SCALE WEIGHT(AT MAX.NET WEIGHT) □ , 20.3910 MG/SQ.CH.

FRACTION OF LIMITING
SCALE WEIGHT

ELAPSED TIME
(HOURS)

.50000	380.54
.90000	2763.42
.95000	4030.56

ALLOY CORROSION
(MG/SQ.CM.)

ELAPSED TIME
(HOURS)

71.90	1623.14
359.50	14062.02
719.00	30093.12

ELAPSED TIME (HOURS)	CORROSION LOSS (MG/SQ.CM.)	SCALE WEIGHT (MG/SQ.CM.)	NET SPECIMAN WEIGHT (MG/SQ.CM.)	CORROSION LOSS (MILLIMETERS)	SCALE THICKNESS (MILLIMETERS)
.31	.7861	1.1387	.3526	.001093	.002186
.69	1.1745	1.6939	.5194	.001633	.003251
.86	1.3119	1.8891	.5773	.001825	.003626
1.11	1.4914	2.1433	.6519	.002074	.004114
1.64	1.8150	2.5989	.7839	.002524	.004988
3.06	2.4855	3.5323	1.0468	.003457	.006780
5.83	3.4429	4.8409	1.3980	.004789	.009292
20.83	6.5841	8.9401	2.3561	.009157	.017160
23.61	7.0209	9.4875	2.4666	.009765	.018210
30.56	8.0169	10.7154	2.6985	.011150	.020567
55.56	10.9254	14.1469	3.2215	.015195	.027153
86.11	13.7390	17.2579	3.5188	.019109	.033124
116.67	16.1290	19.7493	3.6203	.022433	.037906
166.67	19.5088	23.0503	3.5415	.027133	.044242
194.44	21.1960	24.6061	3.4101	.029480	.047229
222.22	22.7849	26.0178	3.2329	.031690	.049938
236.11	23.5482	26.6782	3.1300	.032751	.051206

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TABLE I. - STOICHIOMETRIC FACTOR^a

$$[a = (M_1x + M_2y)/Oz; b = a + 1.]$$

(a) One-metal oxides (b) Two-metal oxides
(i.e., spinels)

Oxide	a	Oxide	a
ThO ₂	7.2512	CoCr ₂ O ₄	2.5458
CoO	3.6831	NiCr ₂ O ₄	2.5423
NiO	3.6694	FeCr ₂ O ₄	2.4977
FeO	3.4906	MnCr ₂ O ₄	2.4834
MnO	3.4338	AlCr ₃ O ₄	2.0466
Fe ₃ O ₄	2.6180	CoAl ₂ O ₄	1.7639
Fe ₂ O ₃	2.3271	NiAl ₂ O ₄	1.7605
Cr ₂ O ₃	2.1667	FeAl ₂ O ₄	1.7158
MoO ₃	1.9988	MnAl ₂ O ₄	1.7016
Al ₂ O ₃	1.1242	CrAl ₂ O ₄	1.6556
CrO ₃	1.0833		
SiO ₂	.8778		

^aFor example, for Cr₂O₃, $a = \frac{(52.00 \times 2) + 0}{16 \times 3} = 2.1667$

and for NiCr₂O₄, $a = \frac{(58.71 \times 1) + (52.00 \times 2)}{16 \times 4} = 2.5423$

TABLE II. - INPUT DATA FOR PREDOMINANTLY Cr₂O₃-FORMING ALLOYS FOR
PARALINEAR OXIDATION ANALYSIS (COREST)

[Scale, Cr₂O₃; stoichiometric constants: $a = 2.1667$, $b = 3.1667$; density of Cr, $\rho_m = 7.19 \text{ g/cm}^3$;
density of Cr₂O₃, $\rho_r = 5.21 \text{ g/cm}^3$.]

Alloy	Test conditions			Before $\Delta\bar{W}$	At $\sim \Delta\bar{W}$	After $\Delta\bar{W}$
	Time, hr	Temper- ature, °C	Number of data points	Test points - input to COREST: time, t , hr; specific sample weight change, ΔW , mg/cm ² ; time to reach $\Delta\bar{W}$, \bar{t} , hr; maxi- mum ΔW in parolinear oxidation, $\Delta\bar{W}$, mg/cm ²		
Alloy A ^a (ref. 6)	1280	1200	31	$t_1 = 100$, $\Delta W_1 = 3.21$ $t_2 = 200$, $\Delta W_2 = 3.59$	$\bar{t} = 294$ $\Delta\bar{W} = 3.62$	$t_1 = 780$, $\Delta W_1 = 2.09$ $t_2 = 1280$, $\Delta W_2 = -0.20$
Cr-0.2Y (ref. 4)	240	1200	17	$t_1 = 30.56$, $\Delta W_1 = 2.50$ $t_2 = 86.11$, $\Delta W_2 = 3.29$	$\bar{t} = 166.70$ $\Delta\bar{W} = 3.48$	$t_1 = 222.22$, $\Delta W_1 = 3.24$ $t_2 = 236.11$, $\Delta W_2 = 3.13$
Ni-40Cr	1020	1200	87	$t_1 = 100$, $\Delta W_1 = 2.859$ $t_2 = 200$, $\Delta W_2 = 3.204$	$\bar{t} = 250$ $\Delta\bar{W} = 3.240$	$t_1 = 400$, $\Delta W_1 = 2.920$ $t_2 = 900$, $\Delta W_2 = 0.669$
Tophet 30 ^b 2-37	2085	1200	55	$t_1 = 100$, $\Delta W_1 = 1.955$ $t_2 = 196$, $\Delta W_2 = 2.249$	$\bar{t} = 225$ $\Delta\bar{W} = 2.297$	$t_1 = 1200$, $\Delta W_1 = 0.875$ $t_2 = 2050$, $\Delta W_2 = -1.061$
Tophet 30 ^b 2-35	2688	1150	71	$t_1 = 40$, $\Delta W_1 = 1.670$ $t_2 = 80$, $\Delta W_2 = 1.871$	$\bar{t} = 110$ $\Delta\bar{W} = 1.957$	$t_1 = 700$, $\Delta W_1 = 1.737$ $t_2 = 2300$, $\Delta W_2 = 0.330$
Tophet 30 ^b 2-42	1850	1150	41	$t_1 = 96$, $\Delta W_1 = 2.012$ $t_2 = 180$, $\Delta W_2 = 2.188$	$\bar{t} = 420$ $\Delta\bar{W} = 2.382$	$t_1 = 990$, $\Delta W_1 = 2.017$ $t_2 = 1800$, $\Delta W_2 = 1.259$

^aNi-20Cr-3Fe-0.4Si.

^bNi-29.6Cr-1.43Si.

TABLE III. - DERIVED PARALINEAR ESTIMATES FROM COREST OUTPUT FOR SIX

 Cr_2O_3 -FORMING ALLOYS FOR THREE TIME STAGES OF INPUT(a) Before $\Delta\bar{W}$

Alloy	Fit, ^a ±mg/cm ²	Parabolic scaling constant, k _p	Linear vaporization constant, k _v	Limiting value of specific weight of metal oxide formed and re- tained, in para- linear oxidation, W _r , lim	Time to reach-	
					ΔW, mg/cm ²	W _m , mg/cm ² (μm)
					0	71.9 (100)
					Time, t, hr	
Alloy A (ref. 6)	1.191	0.2344	0.01833	64.13	899.11	2913.91
Cr-0.2Y (ref. 4)	.156	.3565	.02938	60.83	532.09	1874.00
Ni-40Cr	.345	.1850	.01620	57.26	908.56	3516.48
Tophet 30 2-37	1.841	.08013	.00984	40.85	1067.46	6848.28
Tophet 30 2-35	15.635	.1579	.02368	33.44	362.90	3086.67
Tophet 30 2-42	3.682	.1028	.01322	38.99	758.16	5199.20

(b) At $\Delta\bar{W}$

Alloy A (ref. 6)	0.297	0.1797	0.01397	64.48	1186.21	3 810.58
Cr-0.2Y (ref. 4)	.206	.2929	.02369	61.99	672.59	2 299.64
Ni-40Cr	.243	.1693	.01471	57.72	1008.69	3 856.57
Tophet 30 2-37	2.639	.09453	.01158	40.92	907.82	5 810.11
Tophet 30 2-35	12.426	.1404	.02019	34.86	443.82	3 563.35
Tophet 30	.621	.05446	.00644	42.43	1694.59	10 289.80

(c) After $\Delta\bar{W}$

Alloy A (ref. 6)	0.469	0.1339	0.01179	56.95	124.11	4 845.06
Cr-0.2Y (ref. 4)	.184	.4434	.03397	65.45	495.17	1 553.64
Ni-40Cr	.270	.1578	.01418	55.83	1012.19	4 074.22
Tophet 30 2-37	.352	.03507	.00529	33.21	1612.24	13 839.10
Tophet 30 2-35	.460	.01935	.00313	31.03	2549.98	24 018.00
Tophet 30 2-42	.360	.02698	.00359	37.68	2697.92	19 421.54

^aEstimated error is averaged over whole curve.

TABLE IV. - DERIVED PARALINEAR VALUES FOR PREDOMINANTLY Cr_2O_3 -FORMING ALLOYS WITH GIVEN PARABOLIC SCALINGAND LINEAR VAPORIZATION CONSTANTS COMPARED WITH PARABOLIC OXIDATION ($k_v = 0$)

Temperature, °C	Parabolic scaling constant, k _p , (mg/cm ²) ² /hr	Linear vaporization constant, ^a k _v , mg/cm ² /hr	Metal consumed, W _m , mg/cm ² (Thickness change, μm)			Limiting specific weight of Cr ₂ O ₃ on alloy surface, W _{r, lim} , mg/cm ²	Specific sample weight change (maximum pos- itive value), ΔW̄, mg/cm ²	Time to reach maximum ΔW in paralinear oxidation ΔW̄, t̄, hr	Time to cross zero axis (where ΔW = 0 mg/cm ²), t ₀ , hr	Specific weight of Cr consumed W _m at cross- over time t ₀ , mg/cm ²
			71.9 (100)	359.5 (500)	719 (1000)					
			Time to reach specific weight of Cr consumed per unit area due to oxide buildup and scale vaporization W _m , t, hr							
1000	Low, 0.002	0.00098	96 788	525 702	1 061 845	10.23	0.57	665	2 684	5.70
		.0098	10 618	53 510	107 124	1.02	.06	6.65	26.84	.57
		0	550 592	13 764 810	55 059 241					
	High, 0.05	.00098	19 294	308 580	815 542	255.82	14.36	16 628	67 088	142.45
		.0098	8 155	51 004	104 618	25.58	1.44	166.28	670.88	14.25
		0	22 024	550 589	2 202 370					
1050	Low, 0.0053	0.0021	44 016	244 174	494 375	12.65	0.71	384	1 549	7.05
		.021	4 944	24 960	49 980	1.27	.07	3.84	15.49	.70
		0	207 771	5 194 268	20 777 072					
	High, 0.130	.0021	7 590	129 593	357 600	310.39	17.42	9 415	37 987	172.84
		.021	3 576	23 542	48 562	31.04	1.74	94.15	379.87	17.28
		0	8 471	211 766	847 065					
1100	Low, 0.0122	0.0042	21 555	121 632	246 733	14.56	0.82	221	891	8.11
		.042	2 467	12 475	24 985	1.46	.08	2.21	8.91	.81
		0	90 261	2 256 526	9 026 105					
	High, 0.300	.0042	3 336	59 492	169 463	358.14	20.11	5 432	21 916	199.43
		.042	1 695	11 657	24 167	35.81	2.01	54.32	219.16	19.94
		0	3 671	91 765	367 061					
1150	Low, 0.029	0.0082	10 658	61 913	125 989	17.73	1.00	138	559	9.87
		.082	1 260	6 386	12 794	1.77	.10	1.38	5.59	.99
		0	37 972	949 267	3 797 189					
	High, 0.700	.0082	1 452	27 172	80 435	428.02	24.03	3 325	13 415	238.35
		.082	804	5 886	12 293	42.80	2.40	33.25	134.15	23.83
		0	1 573	39 328	157 312					
1200	Low, 0.056	0.0145	5 918	34 900	71 136	19.36	1.09	85	343	10.78
		.145	711	3 610	7 234	1.94	.11	.85	3.43	1.08
		0	19 664	491 600	1 966 401					
	High, 1.35	.0145	758	14 488	43 667	466.82	26.21	2 051	8 274	259.95
		.145	437	3 302	6 925	46.68	2.62	20.51	82.74	26.00
		0								

^aOxide is Cr_2O_3 ; k_v values represent static and moving air (10 times static air values).

TABLE V. - DIMENSIONLESS TIMES AT CROSSOVER
AND AT MAXIMUM WEIGHT CHANGE

Stoichiometric constant, a	Maximum specific sample weight change, $\bar{N} = \alpha$	Time at maximum sample weight change, $\bar{T} = \beta$	Crossover time, T_0	T_0/\bar{T}
1.0	0.3069	0.1931	0.7969	4.126
1.5	.1558	.1108	.4506	4.066
2.0	.09453	.07213	.2915	4.041
2.5	.06353	.05076	.2044	4.028
3.0	.04565	.03768	.1515	4.021
3.5	.03440	.02909	.1168	4.016
4.0	.02686	.02314	.09288	4.013

TABLE VI. - SUMMARY OF LIMITING VALUES AND
TRENDS OF THE PARALINEAR EQUATIONS

Variable	Limiting value at-			
	Time zero	Time $t = \bar{t}$	Time $t = t_0$	Time $t \gg 1$
t	0	\bar{t}	t_0	$\gg 1$
ΔW	\downarrow	$\Delta \bar{W}$	0	< 0
W_m		\bar{W}_m	> 0	> 0
W_r		\bar{W}_r	> 0	$(b/a)(A/B)$
T		β	$T_0 < a^{-1}$	$\gg 1$
N		α	0	$(1/a) - T$
M		$\beta + (1/b)$	bT_0	$1 + T$
R	\downarrow	$1/b$	aT_0	1
dN/dT	∞	0	$(T_0^{-1} - b)/a$	-1

TABLE VII. - DEFINITION OF PARALINEAR PARAMETERS
AND THEIR CORRESPONDENCE WITH
TRANSPORT COEFFICIENTS

Variable	Definition	Correspondence with transport coefficients
α	$a^{-1} - \ln(b/a)$	-----
β	$\ln(b/a) - b^{-1}$	-----
A	$(\beta/\bar{t})(\Delta W/\alpha)^2$	$a^2 k_p/2$
B	$(\beta/\bar{t})(\Delta W/\alpha)$	ak_v/b
B/A	$\alpha/\Delta\bar{W}$	$2k_v/abk_p$
B^2/A	β/\bar{t}	$2k_v^2/b^2k_p$
W_r, \lim	$(b/a)(A/B)$	$b^2k_p/2k_v$

TABLE VIII. - METHODS FOR CALCULATING
SYSTEM PARAMETERS A AND B

Input data type	Data given	Algorithm citation
1	$\Delta\bar{W}; \bar{t}$	Table VII
2	$k_p; k_v$	Table VII
3	$k_p; \Delta W/t$	Equation (A52)
	$k_v; \Delta W/t$	Equation (A57)
4	$\Delta W_1, t_1; \Delta W_2, t_2$	Equations (A68) and (A69)

TABLE IX. - SUMMARY OF WEIGHT VALUES AT SPECIAL TIMES

Weight	Maximum time, $t = \bar{t}$ and $T = \beta$	Crossover time, $t = t_0$ and $T = T_0$	Limiting time, $t \gg 1$ and $T \gg 1$
M	$\ln(b/a)$	bT_0	$1 + T$
W_m	$\frac{a}{b} \ln(b/a)$	bAT_0/B	$A(1 + T)/B$
R	a^{-2}	aT_0	1
W_r	bA/Ba^2	bAT_0/B	bA/ab

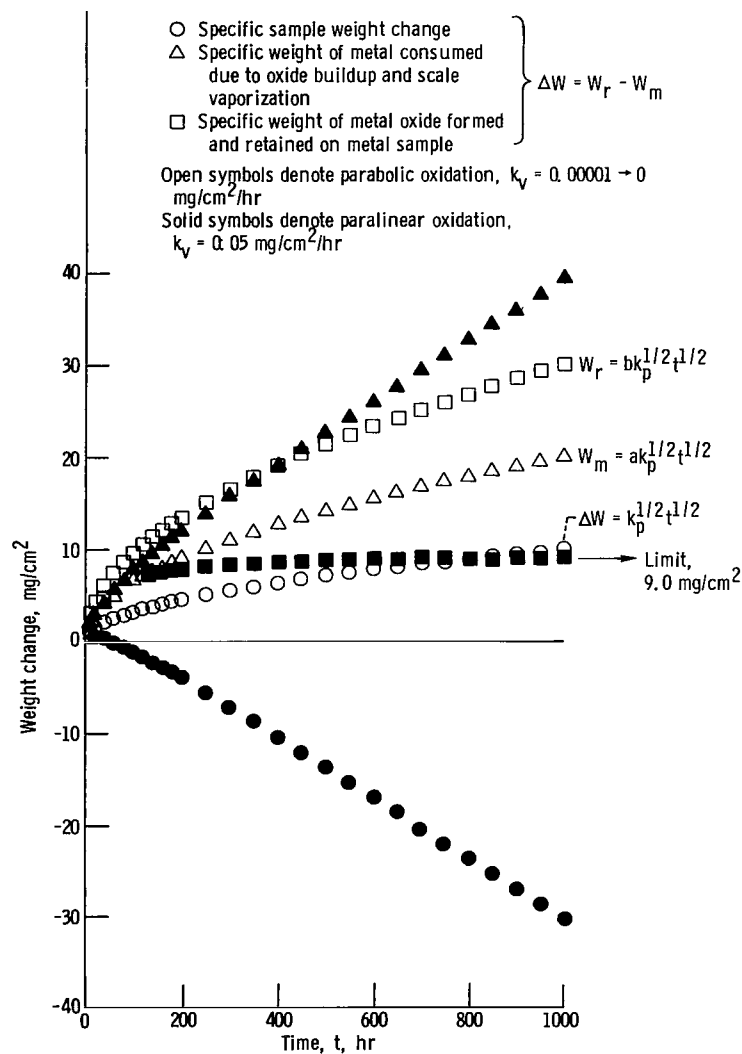


Figure 1. - Comparison of parabolic and paralinear kinetics for hypothetical alloys with the same parabolic scaling constant ($k_p = 0.10 \text{ (mg/cm}^2)^2/\text{hr}$) but different vaporization constants. Stoichiometric constants, $a = 2.0$ and $b = 3.0$.

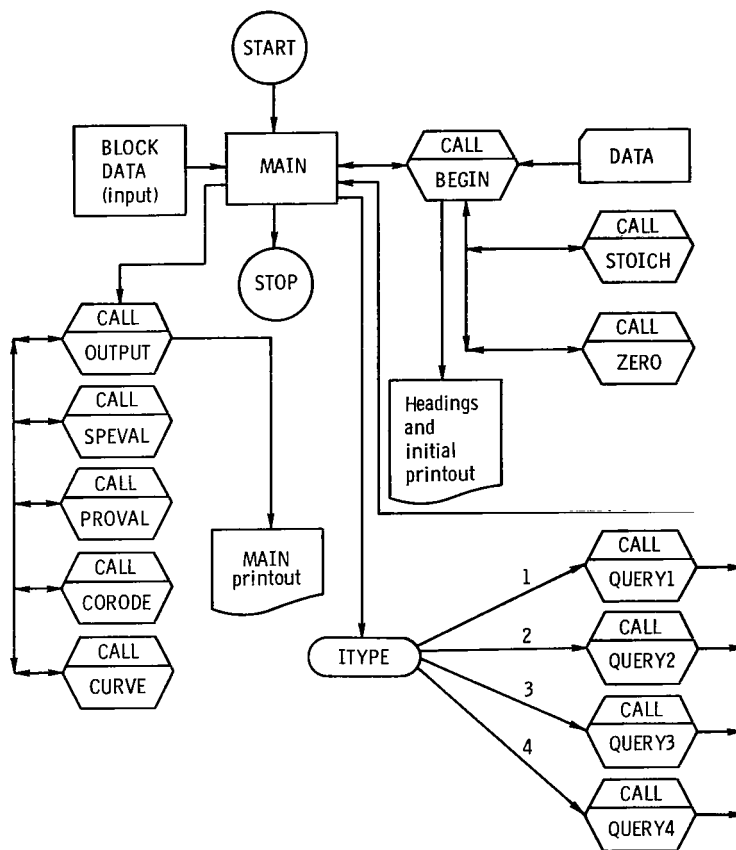


Figure 2. - Flow diagram of COREST, a computer program to analyze paralinear oxidation.

```

Paralinear input - Cr-0.2Y (ref. 4)

BLOCK DATA
C
  DIMENSION HOURS(100),QP(10),XXX(10),TTT(10f0)
  DIMENSION WW(100),TT(100),XKP(100),XKV(100)
C
  COMMON/BLK1/HOURS,QP,XXX,WW,TT
  COMMON/BLK2/ASMLL,BSMALL,DENOX,DENMET
  COMMON/BLK3/ITYPE,LTYPE,LL,LLX,NUMSET,NUMKV,NUMKP
  COMMON/CASE4/XKP,XKV
C
  INPUT FOLLOWS
C
  DATA ASMLL,BSMALL/2.1667,3.1667/
  DATA ITYPE,LL,LLX/4,17,3/
  DATA NUMSET/2/
  DATA QP/.5,.90,.95/
  DATA XXX/71.9,359.5,719.0/
  DATA HOURS/.31,.69,.86,1.11,1.64,3.06,5.83,20.83,23.61,30.56,
  * 55.56,86.11,116.67,194.44,222.22,236.11/
  DATA WW/2.50,3.29,3.24,3.13/
  DATA TT/30.56,86.11,221.22,236.11/
C
  END

FALSE
CHROMIUM OXIDE FORMERS 7.19
CR2O3 TO CRO3 5.21
CR-.2Y TEDMON (REF. 4) BEFORE & AFTER WMAX
12.00 1 ATM.

```

	1A
	2A
Descriptors to title	3A
output listing	4A
	5A

Figure 3. - Typical input data for COREST. Type 4 data; various sets of $\Delta W_1, t_1$ and $\Delta W_2, t_2$.

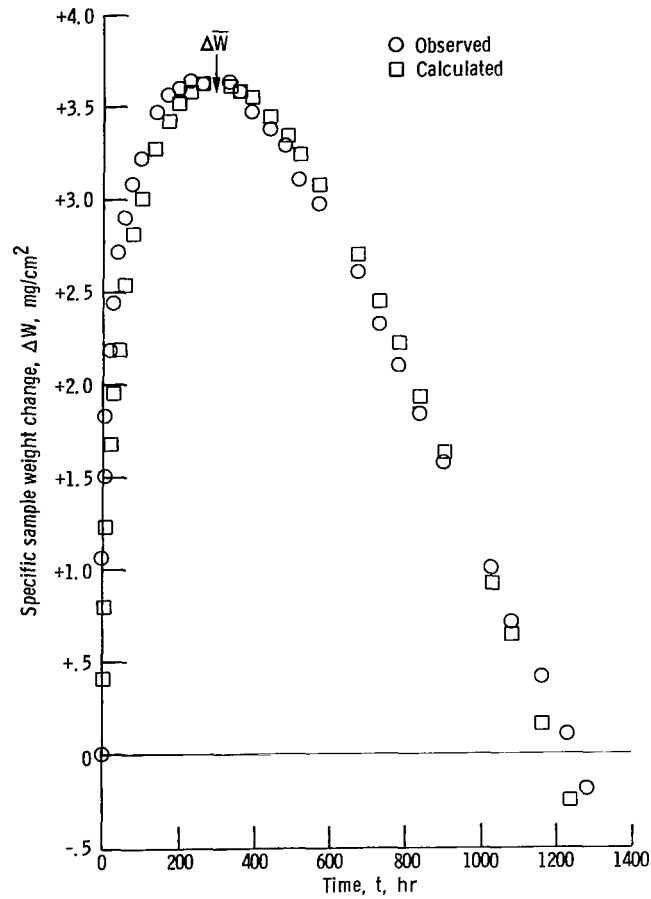


Figure 4. - Specific sample weight change ΔW observed and calculated by parilinear analysis (COREST) for Cr_2O_3 -forming Alloy A (Ni-20Cr-3Fe-0.4Si; ref. 6) at 1200°C . Maximum specific sample weight change in parilinear oxidation, $\Delta \bar{W}$, 3.62 mg/cm^2 ; time to reach $\Delta \bar{W}$, \bar{t} , 294 hr; error estimate, 0.297 mg/cm^2 .

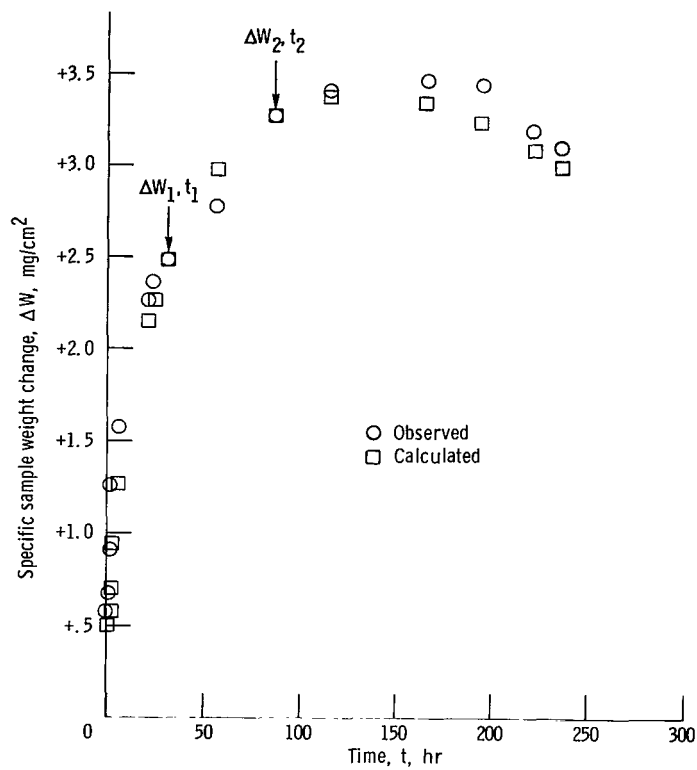


Figure 5. - Specific sample weight change ΔW observed and calculated by parilinear analysis (COREST) for Cr_2O_3 -forming alloy Cr-0.2Y (ref. 4) at 1200°C . $\Delta W_1 = 2.50 \text{ mg/cm}^2$; $\Delta W_2 = 3.29 \text{ mg/cm}^2$; $t_1 = 30.56 \text{ hr}$; $t_2 = 86.11 \text{ hr}$; error estimate, 0.156 mg/cm^2 .

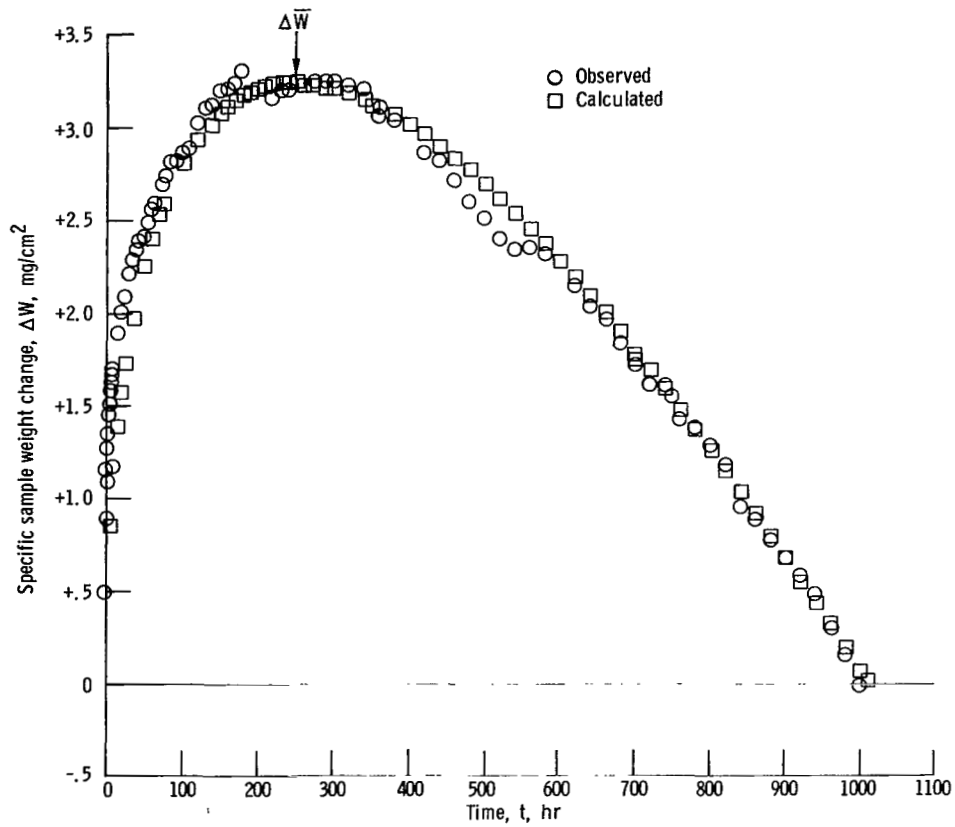


Figure 6. - Specific sample weight change ΔW observed and calculated by paralignear analysis (COREST) for Cr_2O_3 -forming alloy Ni-40Cr at 1200°C . Maximum specific sample weight change in paralignear oxidation, $\Delta \bar{W}$, 3.24 mg/cm^2 ; time to reach $\Delta \bar{W}$, \bar{t} , 250 hr ; error estimate, 0.243 mg/cm^2 ; type 1 input.

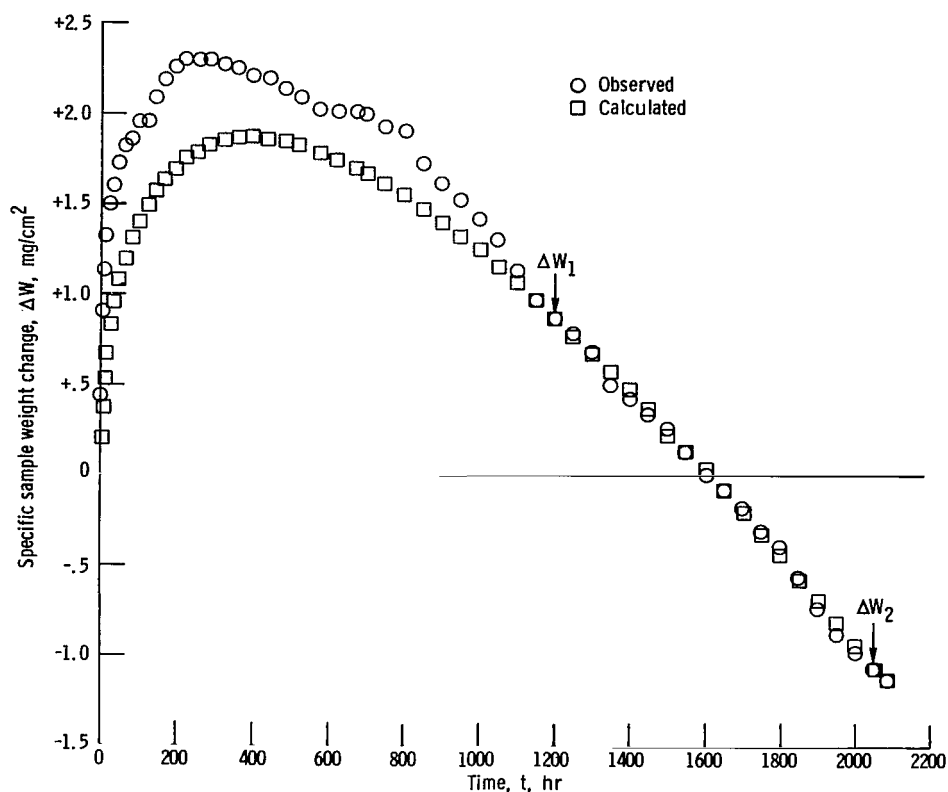


Figure 7. - Specific sample weight change ΔW observed and calculated by parolinear analysis (COREST) for Cr_2O_3 -forming alloy Tophet 30 (2-37) at 1200°C . $\Delta W_1 = 0.875 \text{ mg/cm}^2$; $\Delta W_2 = -1.061 \text{ mg/cm}^2$; $t_1 = 1200 \text{ hr}$; $t_2 = 2050 \text{ hr}$; error estimate, 0.352 mg/cm^2 .

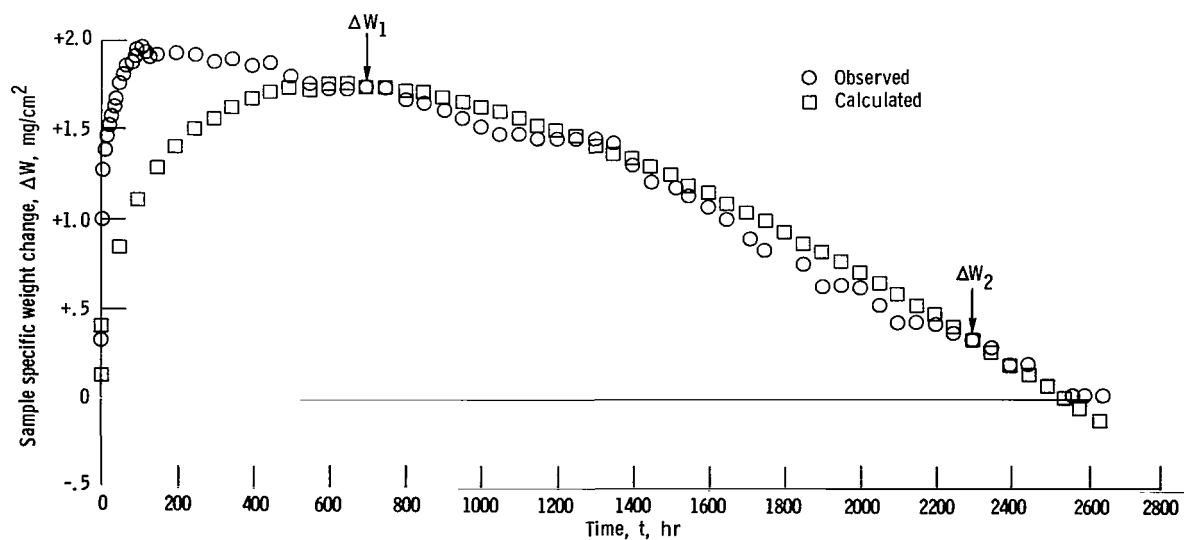


Figure 8. - Specific sample weight change ΔW observed and calculated by parolinear analysis (COREST) for Cr_2O_3 -forming alloy Tophet 30 (2-35) at 1150°C . $\Delta W_1 = 1.737 \text{ mg/cm}^2$; $\Delta W_2 = 0.330 \text{ mg/cm}^2$; $t_1 = 700 \text{ hr}$; $t_2 = 2300 \text{ hr}$; error estimate, 0.460 mg/cm^2 .

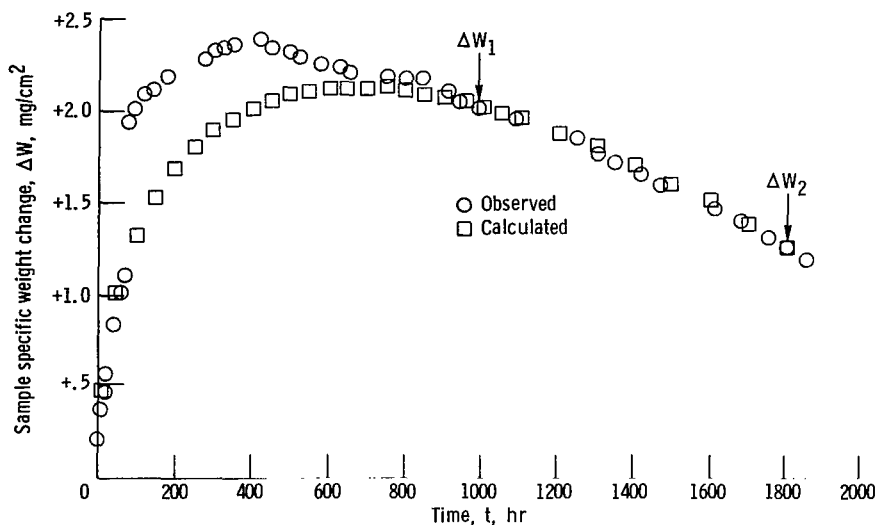


Figure 9. - Specific sample weight change ΔW observed and calculated by parilinear analysis (COREST) for Cr_2O_3 -forming alloy Tophet 30 (2-42) at 1150°C . $\Delta W_1 = 2.017 \text{ mg/cm}^2$; $\Delta W_2 = 1.259 \text{ mg/cm}^2$; $t_1 = 990 \text{ hr}$; $t_2 = 1850 \text{ hr}$; error estimate, 0.360 mg/cm^2 .

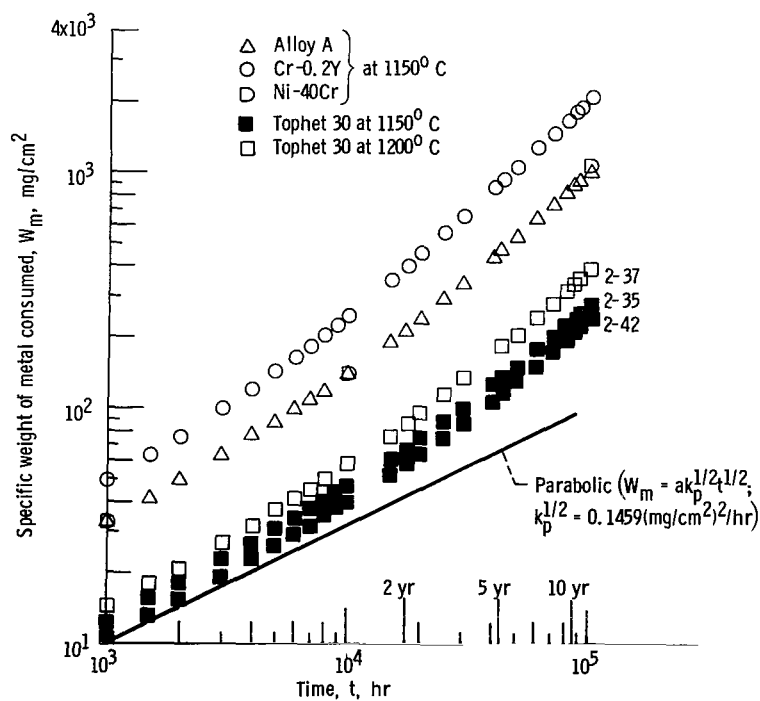


Figure 10. - COREST-calculated specific weight of metal consumed W_m for predominantly Cr_2O_3 -forming alloys above 1100°C , assuming parilinear oxidation. Stoichiometric constant, a , 2.1667.

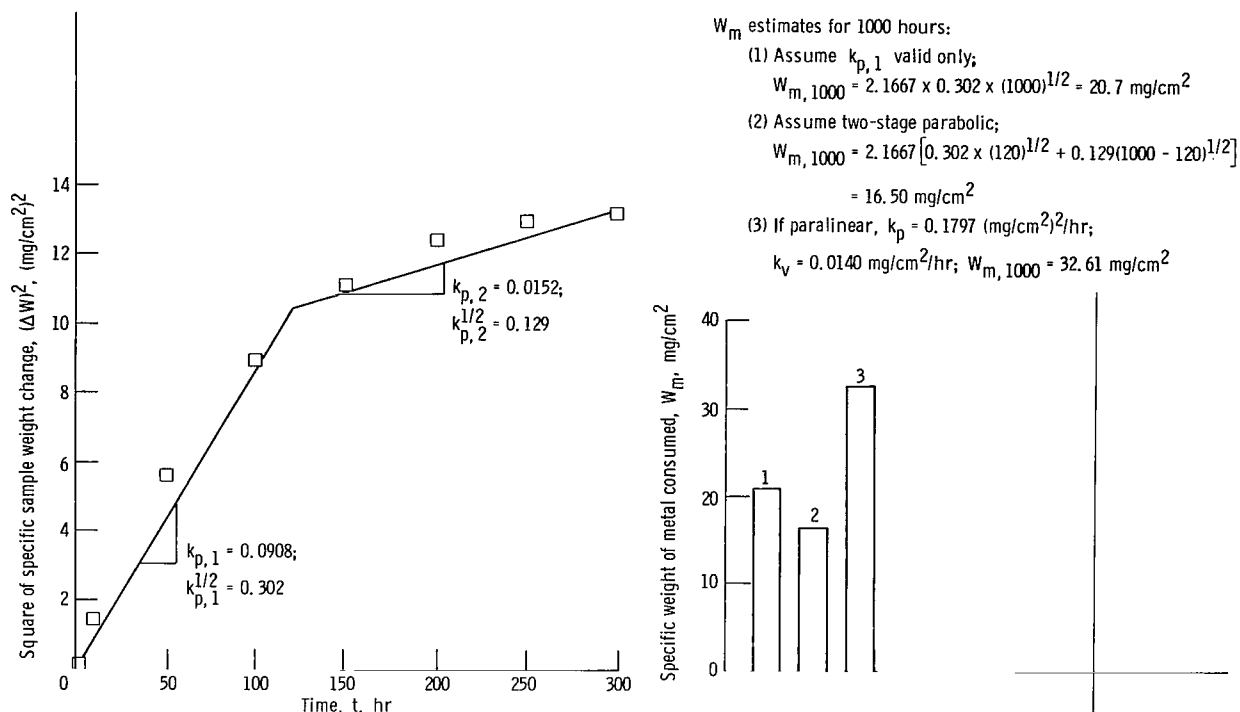


Figure 11. - Comparison of corrosion estimates (specific weight of metal consumed W_m at 1000 hr) if Cr_2O_3 -forming Alloy A (ref. 6) were analyzed from 300-hour data, assuming parabolic rates. $W_m = ak_p^{1/2}t^{1/2}$; $a = 2.1667$ for Cr_2O_3 .

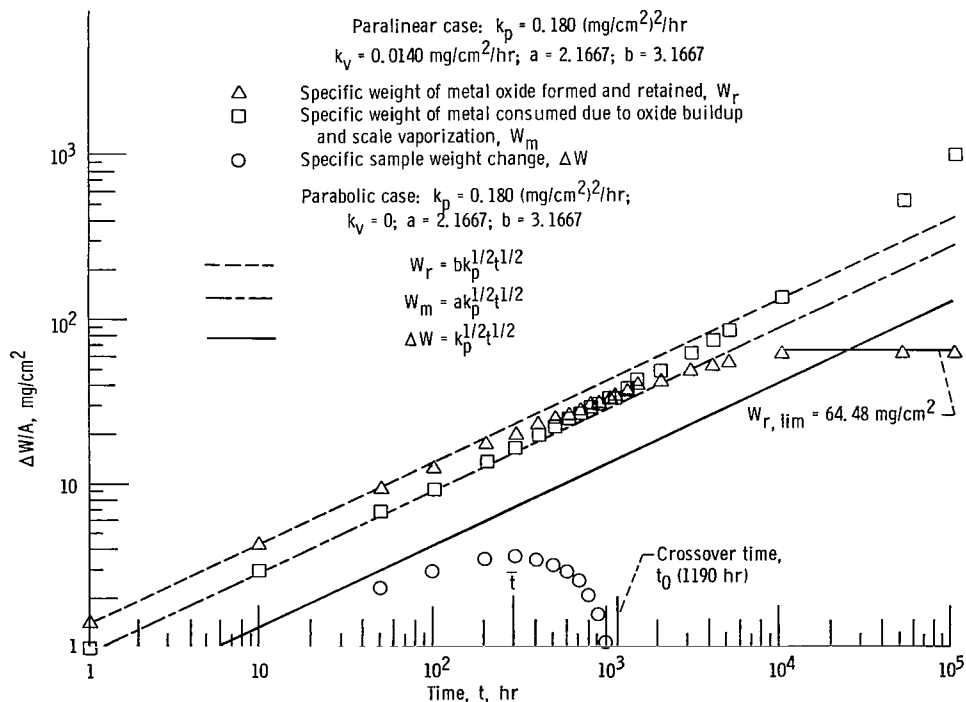


Figure 12. - Comparison of COREST-calculated parilinear and parabolic oxidation results for Cr_2O_3 /chromite-forming Alloy A at 1200°C, for same parabolic scaling constant k_p . Based on input data from reference 6.

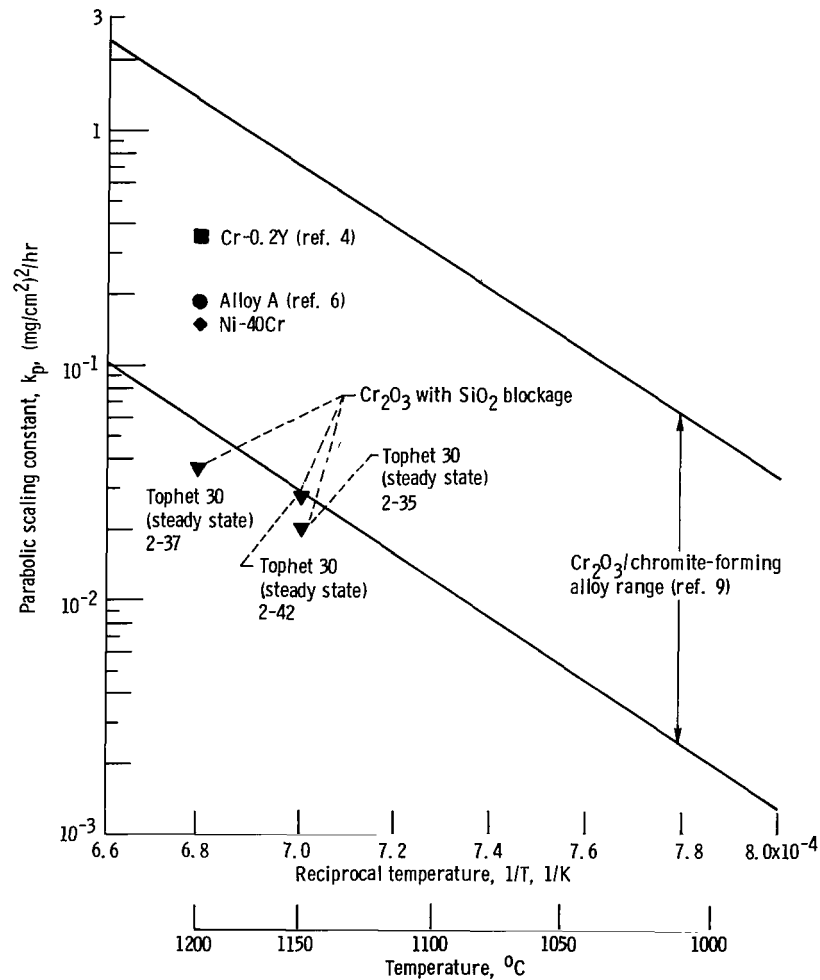


Figure 13. - Parabolic scaling constants calculated by COREST, using paralinear analysis of literature and this study data, as function of reciprocal of absolute temperature.

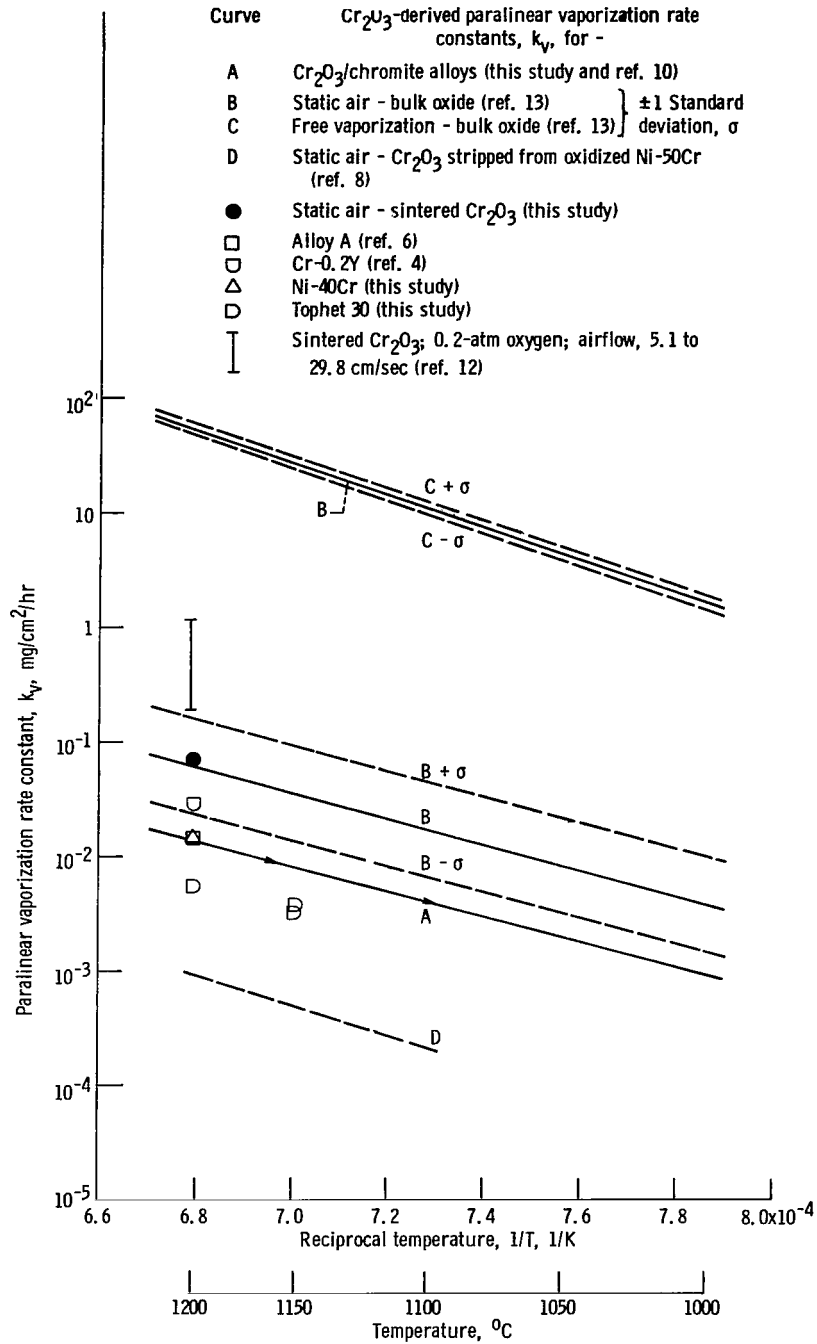


Figure 14. - COREST-calculated vaporization rate constants for Cr_2O_3 as function of reciprocal of absolute temperature, assuming paralineer oxidation of Cr_2O_3 -forming alloys.

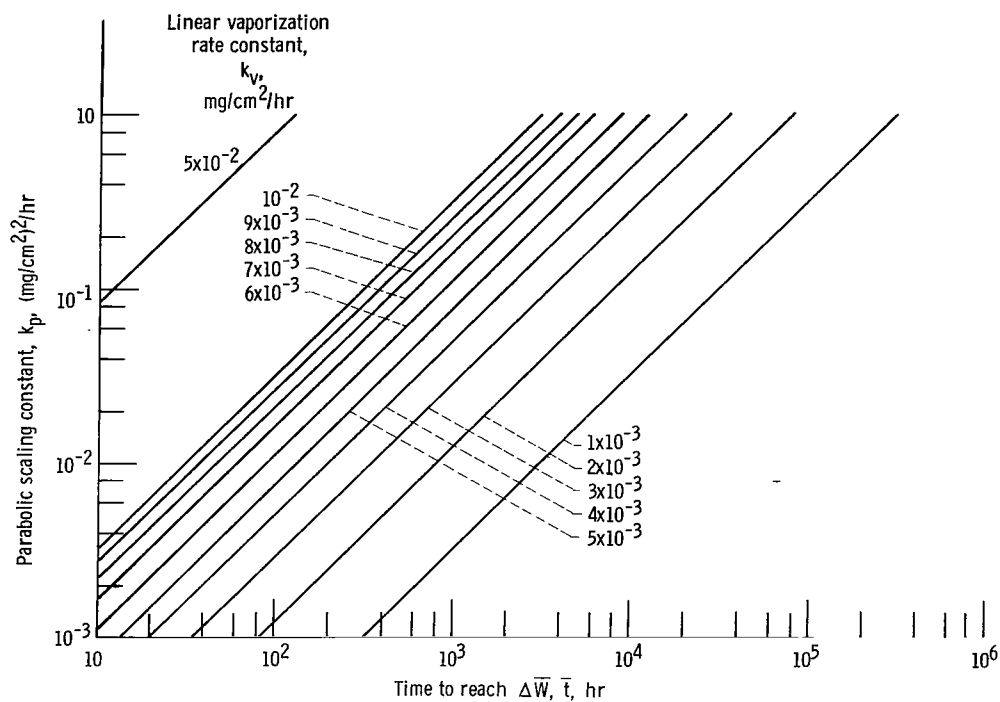


Figure 15. - Time to reach maximum sample specific weight change in parilinear oxidation for various vaporization rate constants as function of typical parabolic scaling constants for Cr_2O_3 /chromite-forming alloys. (In order to detect obvious parilinear behavior, run test to twice \bar{t} time for an apparent vaporization rate constant.)

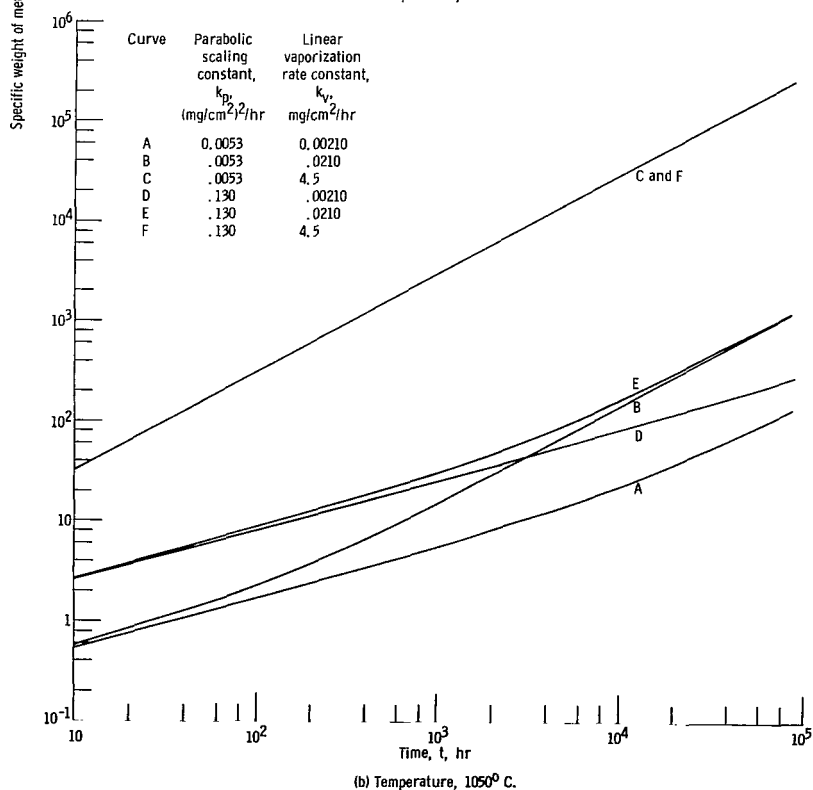
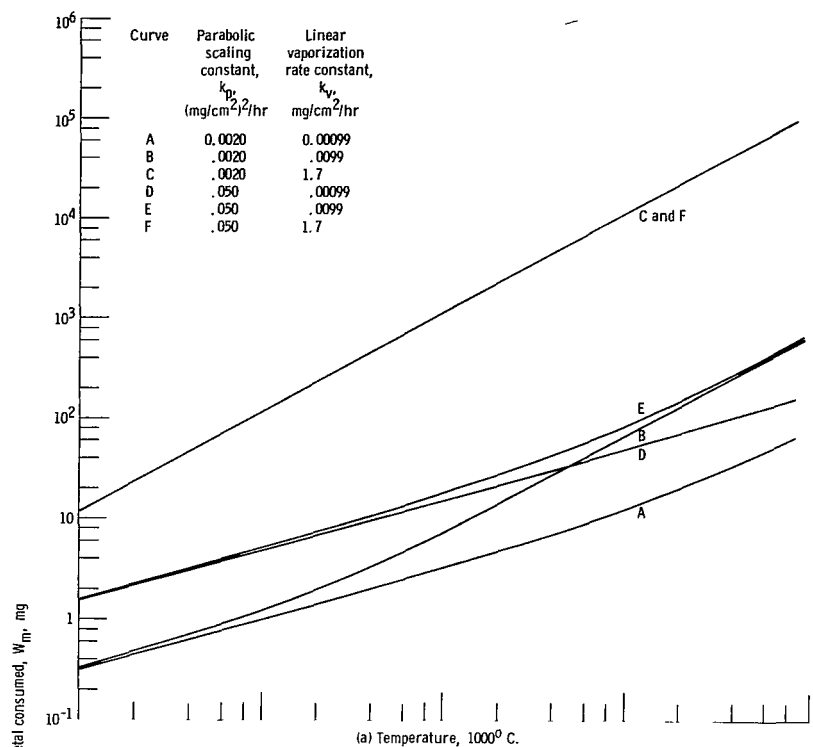


Figure 16. - COREST-calculated specific weight of metal (Cr) consumed in parolinear oxidation for Cr_2O_3 /chromite-forming alloys for high and low parabolic scaling constant limits (from fig. 13) with three levels of linear vaporization scaling constant representing static air, moving air, and free vaporization, respectively.

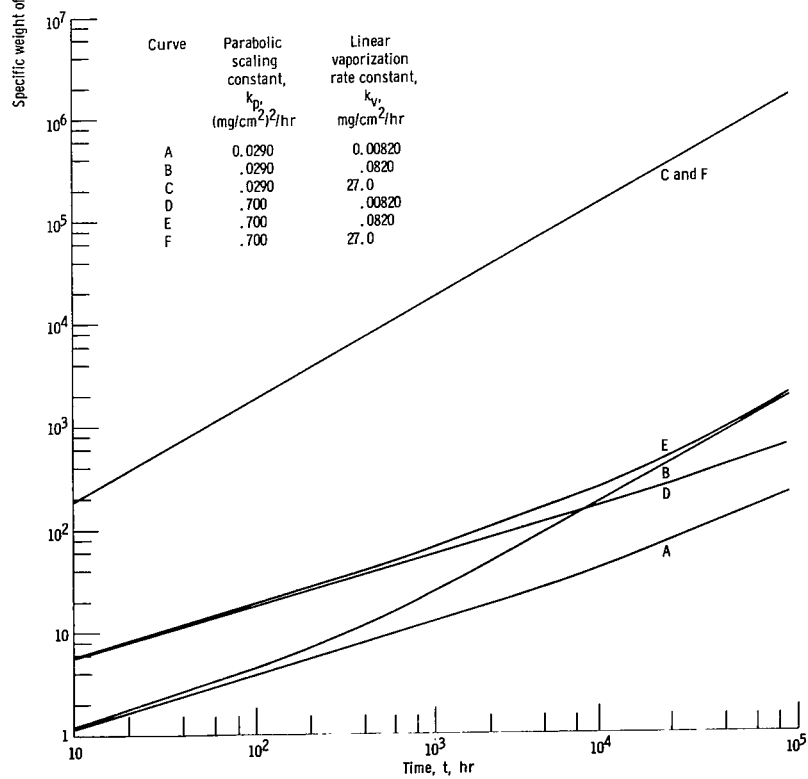
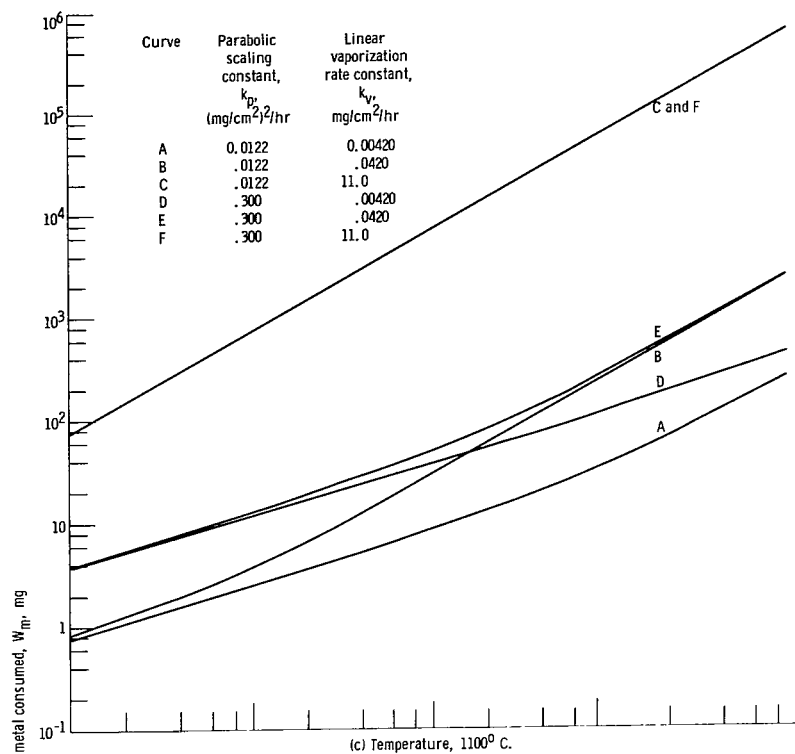
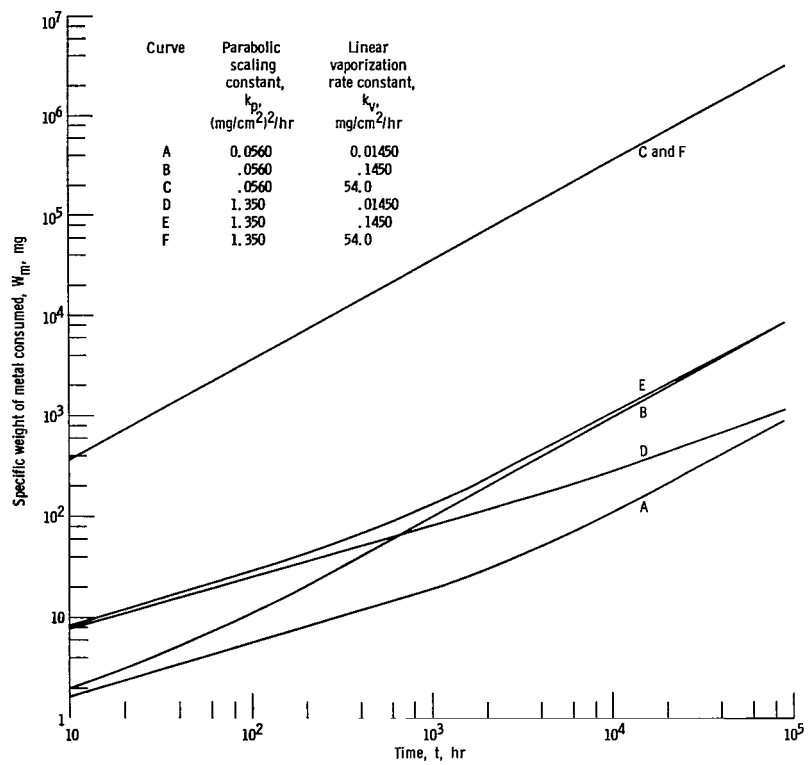


Figure 16. - Continued.



(e) Temperature, 1200° C.

Figure 16. - Concluded.

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